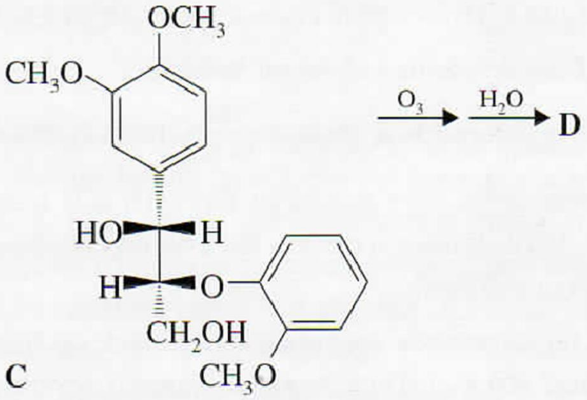
***15.56** Ligninde çok, sık rastlanan birim olan **C** bileşiği model olarak kullanıldığında, C ozonlanırsa **D** elde edilir. Değişik yollarla, böyle bir lignin biriminin üç karbon yan zincirinin stereokimyasının, böyle bir yükseltgenme esnasında tamamen değişmeden kaldığı tespit edilmiştir.

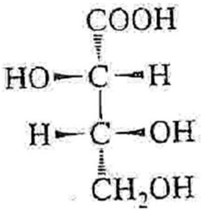


C

GC/MS'de, **D** $M^{+\cdot}$'sı 424 m/z olan tetrakis(*O*-trimetilsilil) türevine dönüştürülmüştür. **D**'nin İR spektrumu 3000 cm^{-1}'de (geniş, kuvvetli) ve 1710 cm^{-1}'de (kuvvetli) bandlar içerir. **D**'nin ^{1}H NMR spektrumu, D_2O ile etkileştirildikten sonra, δ 3,7 de (çoklu 3H) ve δ 4,2 de (ikili, 1H) içermektedir. DEPT ^{13}C NMR spektrumları δ 64 (CH_2), δ 75 (CH), δ 82 (CH) ve δ 177'de (C) sinyaller vermiştir.

D'nin yapısını stereokimyasıyla birlikte bulunuz?

*15.56



(Threonic acid)

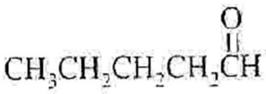
Ozonolysis oxidatively degrades the aromatic rings, leaving only the carboxyl carbon as a remnant of the alkyl substituted benzene ring. Water is an alternative to HOAc used to work up the ozonolysis reaction.

Aldehitler ve Ketonlar I. Karbonil Grubuna Nükleofilik Katılma

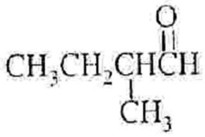
Problem 16.1

(a) $C_5H_{10}O$ Formülüne sahip yedi izomerik aldehit ve ketonun IUPAC türetme adlarını yazınız. (b) C_8H_8O formülüne sahip ve bir benzen halkası içeren tüm aldehit ve ketonların yapılarını ve adlarını (yaygın ve IUPAC türetme adlarını) yazınız.

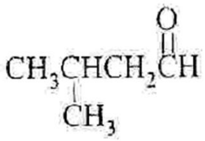
16.1 (a)


$CH_3CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}H$

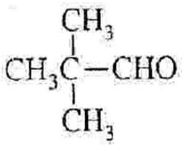
Pentanal


$CH_3CH_2\underset{\underset{CH_3}{|}}{C}H\overset{\overset{O}{\|}}{C}H$

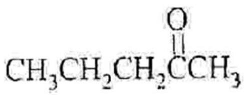
2-Methylbutanal


$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2\overset{\overset{O}{\|}}{C}H$

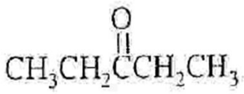
3-Methylbutanal


$CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CHO$

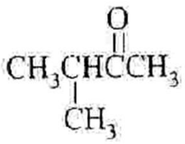
2,2-Dimethylpropanal


$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3$

2-Pentanone

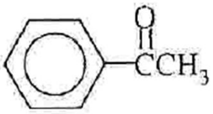

$CH_3CH_2\overset{\overset{O}{\|}}{C}CH_2CH_3$

3-Pentanone

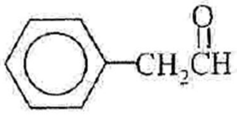

$CH_3\underset{\underset{CH_3}{|}}{C}H\overset{\overset{O}{\|}}{C}CH_3$

3-Methyl-2-butanone

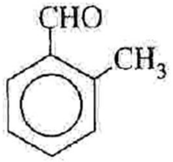
(b)



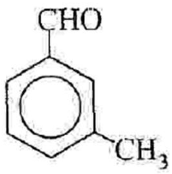
Acetophenone or
methyl phenyl ketone



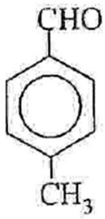
Phenylethanal or
phenylacetaldehyde



2-Methylbenzaldehyde
(*o*-tolualdehyde)



3-Methylbenzaldehyde
(*m*-tolualdehyde)



4-Methylbenzaldehyde
(*p*-tolualdehyde)

Problem 16.2 ➤ Aşağıda verilen bileşik çiftlerinin her birinde hangi bileşik daha yüksek kaynama noktasına sahiptir.
(Bu problemle ilgili çizelgeye bakmadan cevaplayınız)

(a) Pentanal veya 1-Pentanol
(b) 2-Pentanon veya 2-Pentanol
(c) Pentan veya pentanal
(d) Asetofenon veya 2-feniletanol
(e) Benzaldehit veya benzil alkol

16.2 (a) 1-Pentanol, because its molecules form hydrogen bonds to each other.

(b) 2-Pentanol, because its molecules form hydrogen bonds to each other.

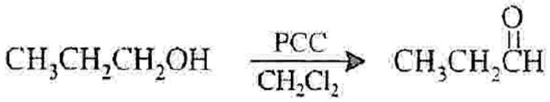
(c) Pentanal, because its molecules are more polar.

(d) 2-Phenylethanol, because its molecules form hydrogen bonds to each other.

(e) Benzyl alcohol because its molecules form hydrogen bonds to each other.

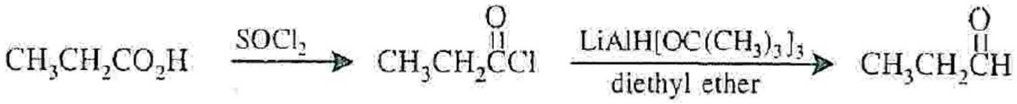
Aşağıdakilerin her birinden propanali nasıl sentezleyebileceğinizi gösteriniz: (a) 1-propanol ve (b) propanoik asit ($CH_3CH_2CO_2H$). ➤ **Problem 16.3**

16.3 (a)



$CH_3CH_2CH_2OH \xrightarrow[CH_2Cl_2]{PCC} CH_3CH_2\overset{\overset{O}{\|}}{C}H$

(b)

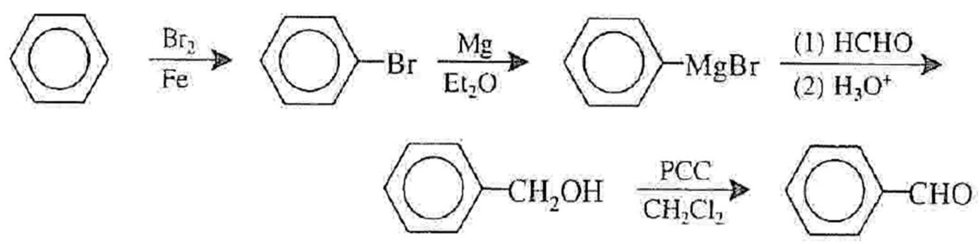


$CH_3CH_2CO_2H \xrightarrow{SOCl_2} CH_3CH_2\overset{\overset{O}{\|}}{C}Cl \xrightarrow[\text{diethyl ether}]{LiAlH[OC(CH_3)_3]_3} CH_3CH_2\overset{\overset{O}{\|}}{C}H$

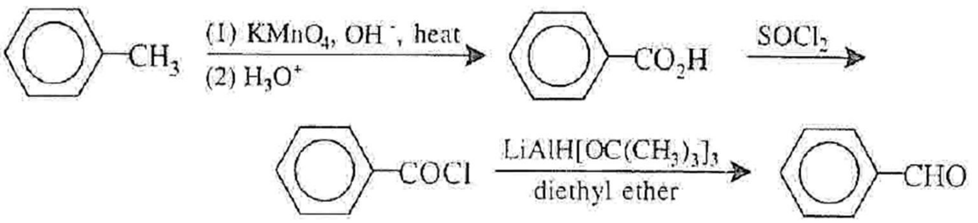
Problem 16.4 ➤ Aşağıdaki tepkimelerin her birini gerçekleştirmek için hangi reaktifleri kullanırdınız?

(a) Benzen ⟶ bromobenzon ⟶ fenilmagnezyum bromür ⟶ benzil alkol ⟶ benzaldehit
(b) Toluen ⟶ benzoik asit ⟶ benzoil klorür ⟶ benzaldehit
(c) Etil bromür ⟶ 1-bütin ⟶ bütanon
(d) 2-Bütin ⟶ bütanon
(e) 1-Feniletanol ⟶ asetofenon
(f) Benzen ⟶ asetofenon
(g) Benzoil klorür ⟶ asetofenon
(h) Benzoik asit ⟶ asetofenon
(i) Benzil bromür ⟶ $C_6H_5CH_2CN$ ⟶ 1-fenil-2-bütanon
(j) $C_6H_5CH_2CN$ ⟶ 2-feniletanol
(k) $CH_3(CH_2)_4CO_2CH_3$ ⟶ heksanal

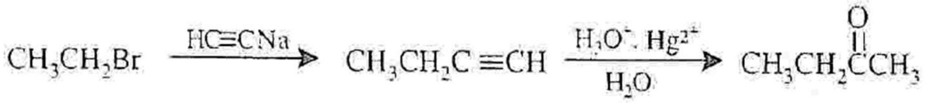
16.4 (a)



(b)

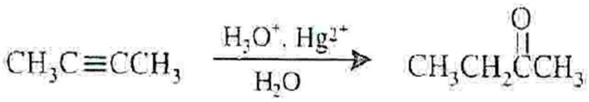


(c)



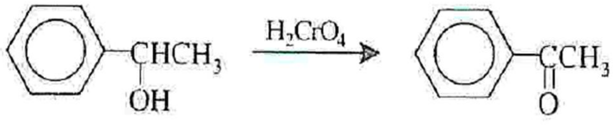
$$CH_3CH_2Br \xrightarrow{HC\equiv CNa} CH_3CH_2C\equiv CH \xrightarrow[H_2O]{H_3O^+,\ Hg^{2+}} CH_3CH_2\overset{\overset{O}{\|}}{C}CH_3$$

(d)

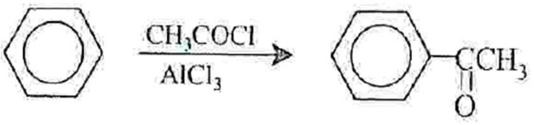


$$CH_3C\equiv CCH_3 \xrightarrow[H_2O]{H_3O^+,\ Hg^{2+}} CH_3CH_2\overset{\overset{O}{\|}}{C}CH_3$$

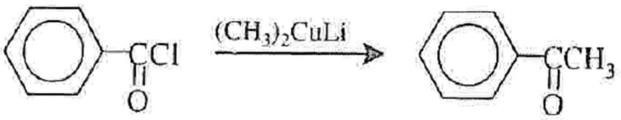
(e)



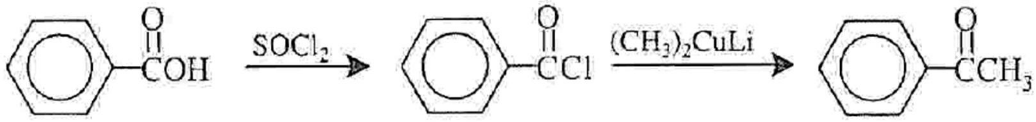
(f)



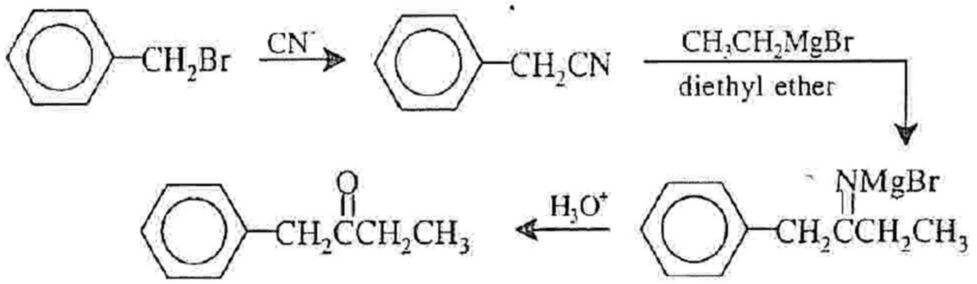
(g)



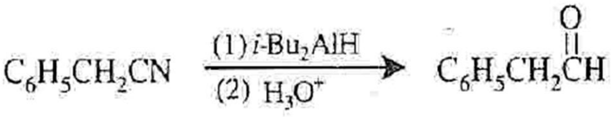
(h)



(i)

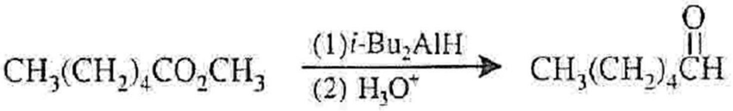


(j)



$$C_6H_5CH_2CN \xrightarrow[(2)\ H_3O^+]{(1)\ i\text{-}Bu_2AlH} C_6H_5CH_2\overset{\overset{O}{\|}}{C}H$$

(k)

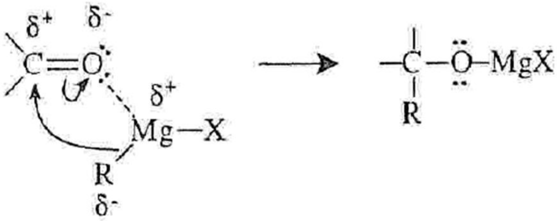


$$CH_3(CH_2)_4CO_2CH_3 \xrightarrow[(2)\ H_3O^+]{(1)\ i\text{-}Bu_2AlH} CH_3(CH_2)_4\overset{\overset{O}{\|}}{C}H$$

Problem 16.5 ➤ Bir aldehit veya ketonun bir Grignard reaktifiyle (Altbölüm 12.8) tepkimesi karbon-oksijen ikili bağına bir nükleofilik katılmadır. (a) Nükleofil nedir? (b) Grignard reaktifinin magnezyum kısmı bu tepkimede önemli bir görev yapar. Bu görev nedir? (c) Başlangıçta hangi ürün oluşur? (d) Su ilave edildiğinde oluşan ürün nedir?

16.5 (a) The nucleophile is the negatively charged carbon of the Grignard reagent *acting as a carbanion.*

(b) The magnesium portion of the Grignard reagent acts as a Lewis acid and accepts an electron pair of the carbonyl oxygen. This acid-base interaction makes the carbonyl carbon even more positive and, therefore, even more susceptible to nucleophilic attack.



(c) The product that forms initially (above) is a magnesium derivative of an alcohol.

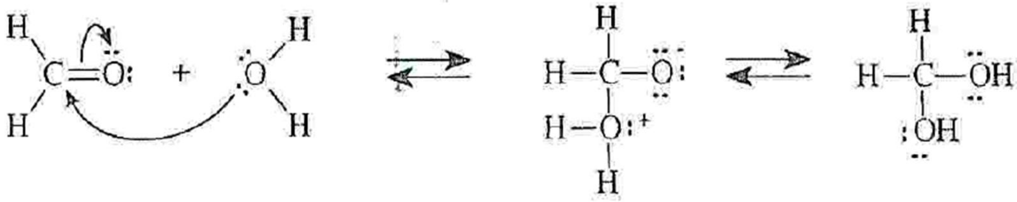
(d) On addition of water, the organic product that forms is an alcohol.

Problem 16.6 ➤ Aldehit ve ketonların $LiA1H_4$ ve $NaBH_4$ (Altbölüm 12.3) ile tepkimeleri karbonil grubuna nükleofilik katılmalardır. Bu tepkimelerde nükleofil nedir?

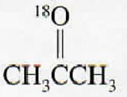
16.6 The nucleophile is a hydride ion.

Formaldehitin suda çözülmesiyle, başlıca *ikiz*-diol, $CH_2(OH)_2$, içeren bir çözelti oluşur. Formaldehitten bu *ikiz*-diolün oluşumundaki basamakları gösteriniz. ◀ **Problem 16.7**

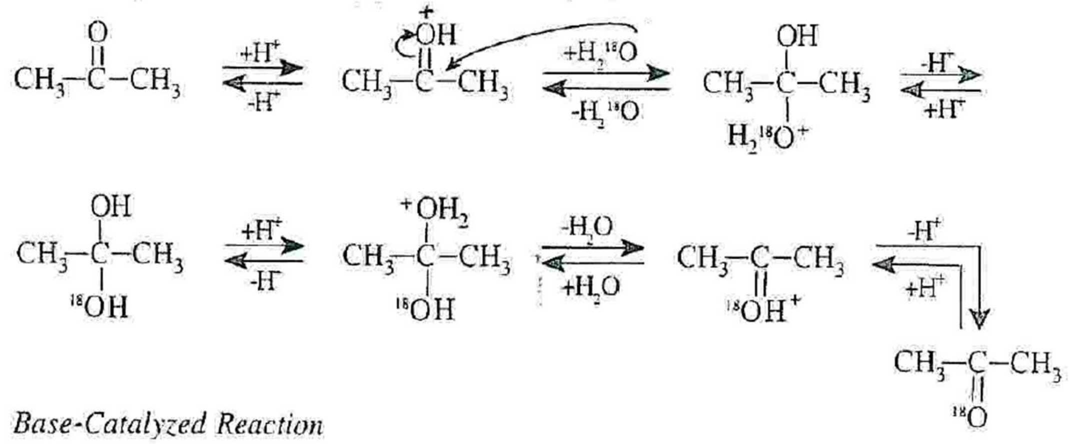
16.7



Aseton, normal ^{16}O yerine ^{18}O içeren suda (yani, $H_2{}^{16}O$ yerine $H_2{}^{18}O$'de) ◀ **Problem 16.8**

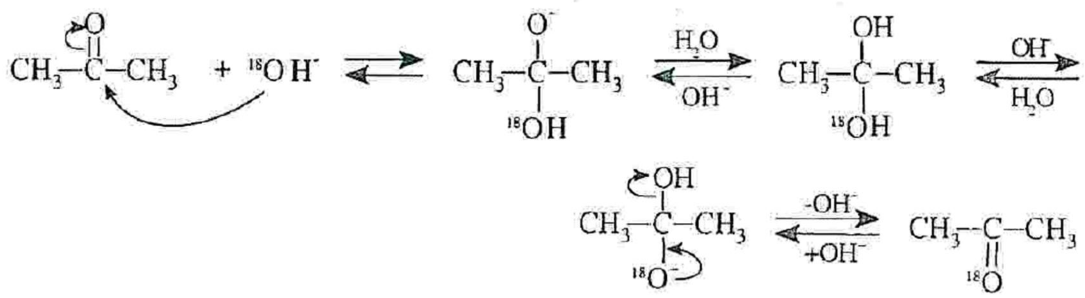
çözüldüğünde, aseton kısa sürede ^{18}O kazanmaya başlar ve  $CH_3\overset{\overset{^{18}O}{\|}}{C}CH_3$ oluşur. Bu oksijeni etiketli asetonun oluşması eser miktardaki kuvvetli asitler ve kuvvetli bazlar (OH^- gibi) tarafından katalizlenir. Asit-katalizli ve baz-katalizli bu tepkimelerin her ikisini de açıklayan basamakları gösteriniz?

16.8 *Acid-Catalyzed Reaction*

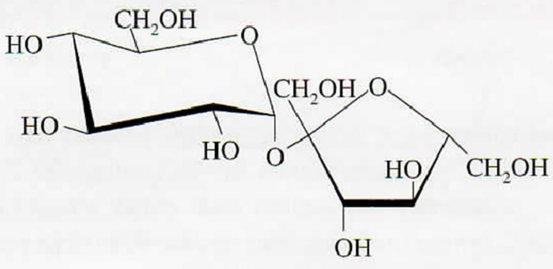


Base-Catalyzed Reaction

$$OH^- + H_2{}^{18}O \rightleftharpoons H_2O + {}^{18}OH^-$$

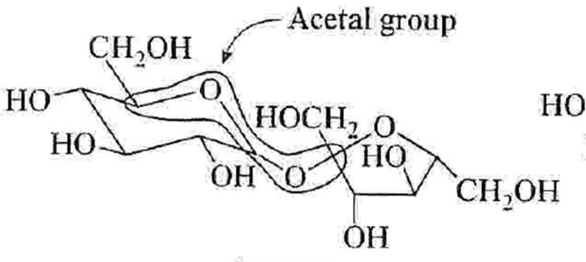


Problem 16.9 ➤ Aşağıda gösterilen yapı formülü sukroza (sofra şekeri) aittir. Sukroz iki asetal gruba sahiptir. Bunları belirleyiniz.

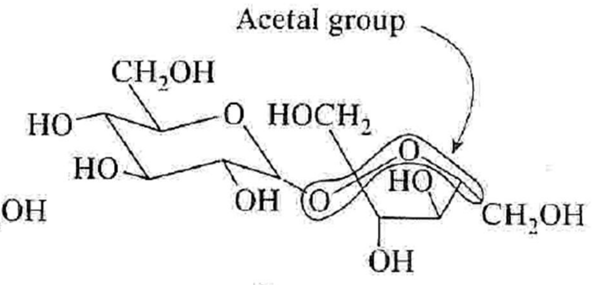


Sukroz (Sakkaroz)

16.9



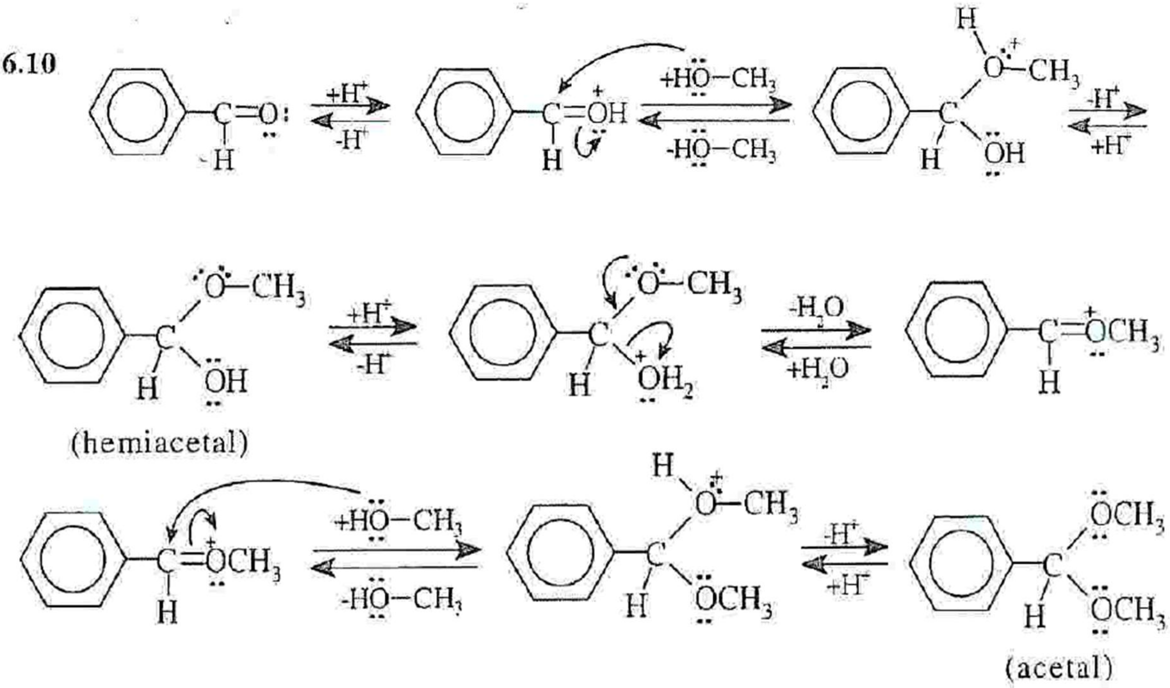
Sucrose



Sucrose

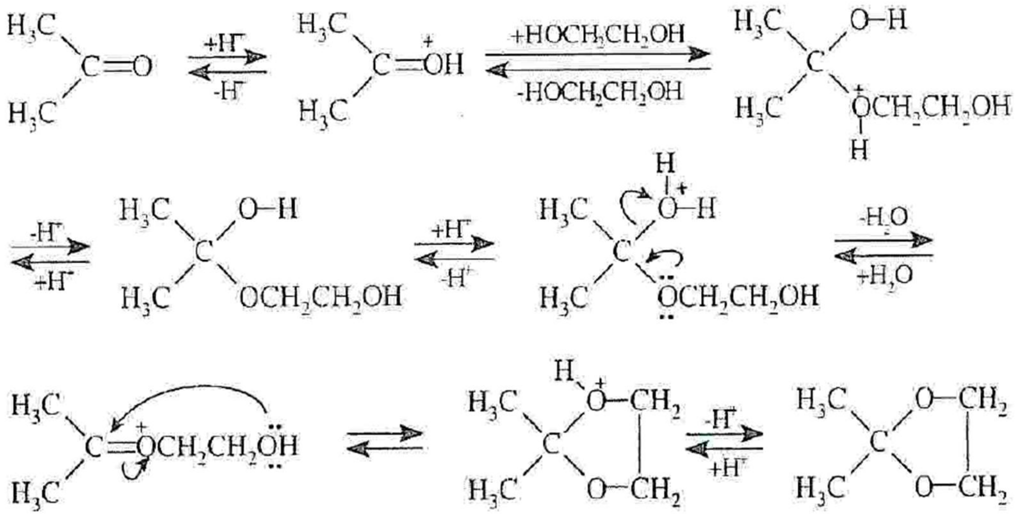
Benzaldehit ve metanolden, bir asit katalizör varlığında asetal oluşumu için ayrıntılı bir mekanizma yazınız. ◄ **Problem 16.10**

16.10

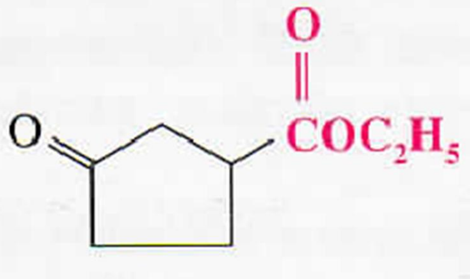


Problem 16.11 ➤ Aseton ve etilen glikolden, HC1 gazı varlığında, halkalı asetal oluşum mekanizmasının bütün basamaklarını gösteriniz.

16.11

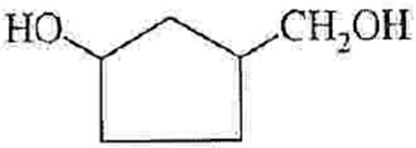


Problem 16.12 ➤ Eğer **A**, halkalı asetale çevrilmeden lityum alüminyum hidrür ile etkileştirilseydi hangi ürün elde edilirdi?



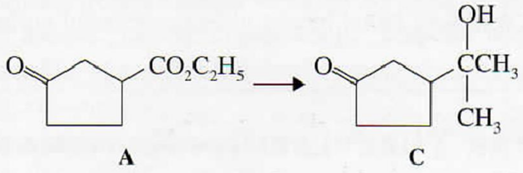
A

16.12



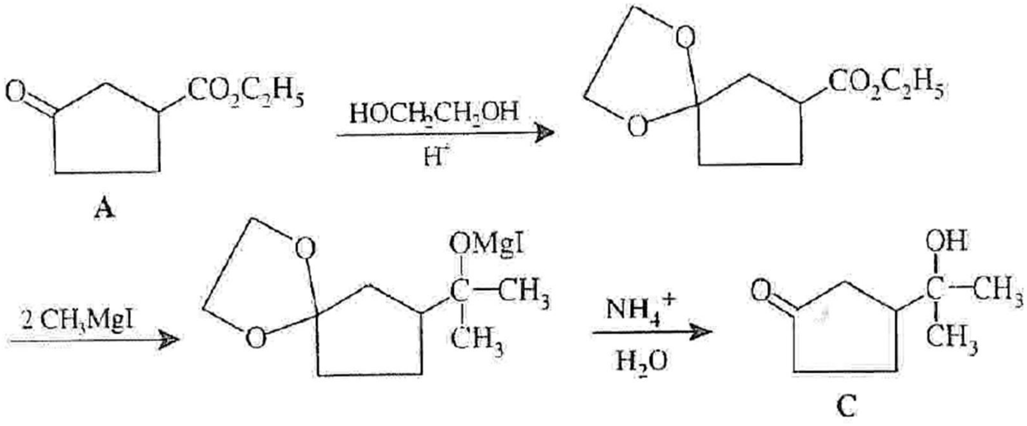
Problem 16.13

(a) Aşağıdaki dönüşümü yapabilmek için bir halkalı asetali nasıl kullanabileceğinizi gösteriniz.

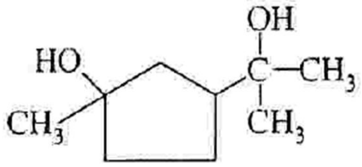


(b) Metilmagnezyum bromürün doğrudan **A**'ya katılması neden **C**'yi oluşturmada başarısız olur?

16.13 (a)

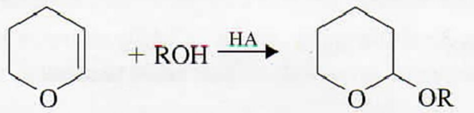


(b) Addition would take place at the ketone group as well as at the ester group. The product (after hydrolysis) would be.



Problem 16.14

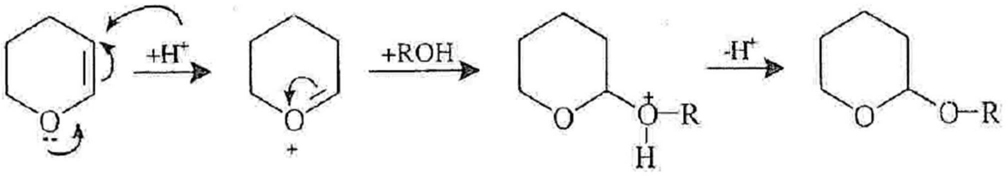
Dihidropiran, eser miktarda susuz HC1 veya H_2SO_4 varlığında bir alkolle kolayca tepkimeye girerek bir tetrahidropironil (THP) eter oluşturur.



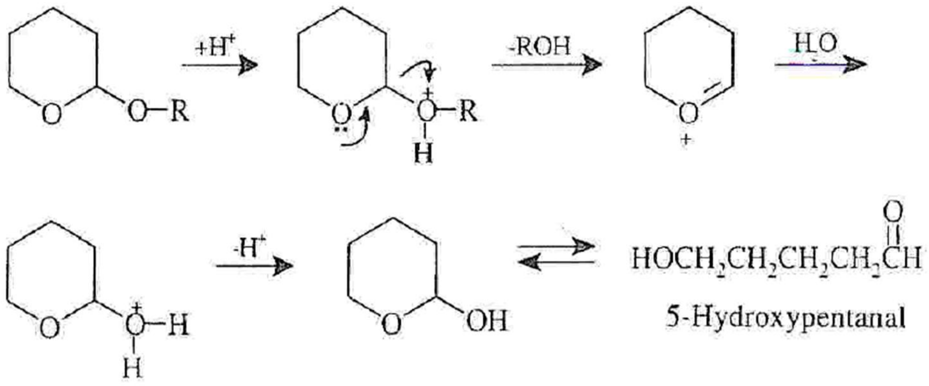
ihidropiran **Tetrahidropiranil eter**

(a) Bu tepkime için uygun bir mekanizma yazınız. (b) Tetrahidropiranil eterler sulu bazlarda kararlıdırlar fakat sulu asitlerde hızla hidrolize uğrayarak başlangıç alkolünü ve diğer bir bileşiği verirler. Açıklayınız. (Diğer bileşik nedir?) (c) Tetrahidropiranil grubu alkol ve fenoller için koruyucu grup olarak kullanılabilir. 4-Kloro-1-bütanol ile başlayarak yapılan 5-metil-1,5-heksandiol sentezinde bu grubu nasıl kullanabileceğinizi gösteriniz.

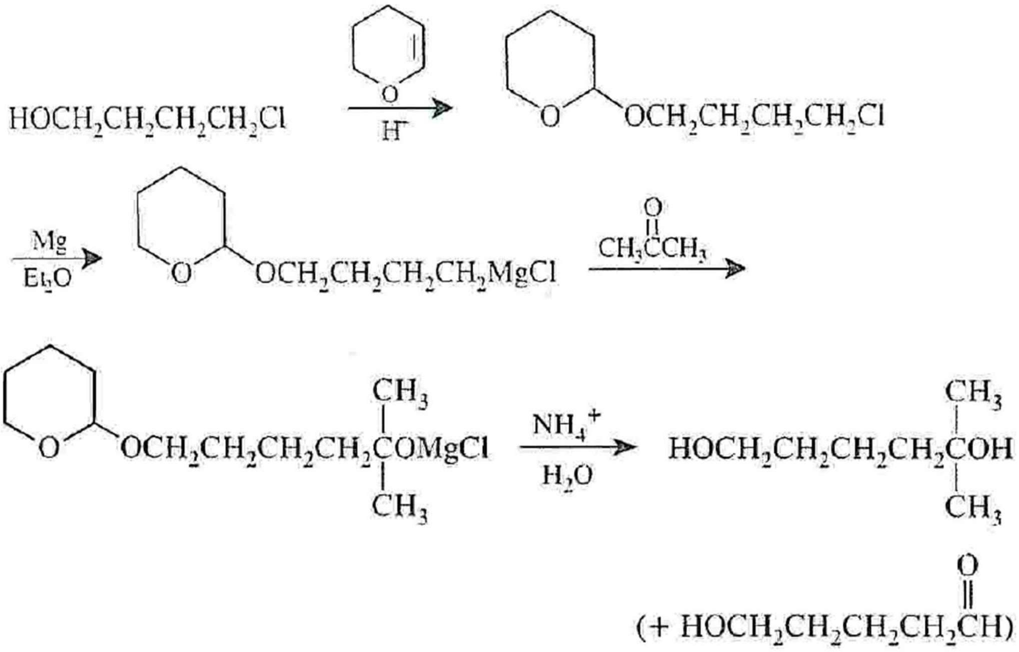
16.14 (a)



(b) Tetrahydropyranyl ethers are acetals; thus, they are stable in aqueous base and hydrolyze readily in aqueous acid.

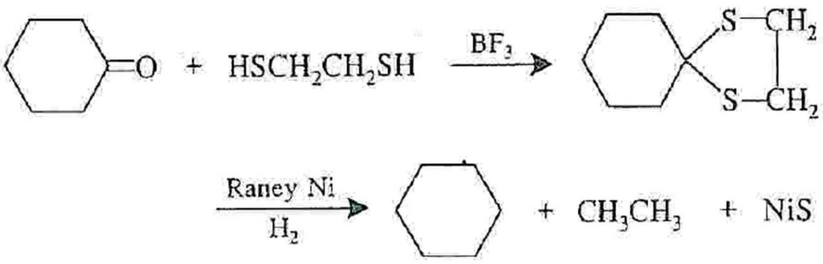


(c)

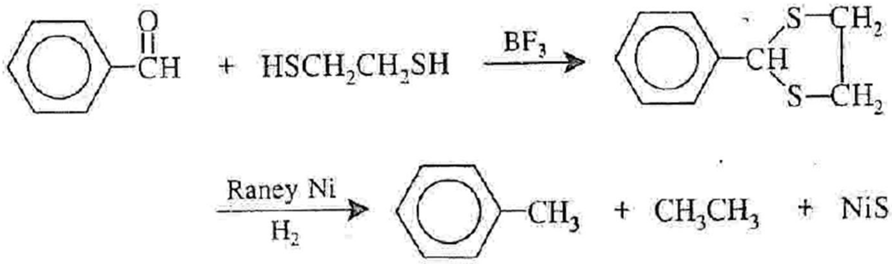


Problem 16.15 ➤ (a) Sikloheksanonun sikloheksanole (b) benzaldehitin toluene dönüştürülmesinde tiyoasetal oluşumu ve Raney Nikel kükürt gidermesini nasıl kullanabileceğinizi gösteriniz.

16.15 (a)

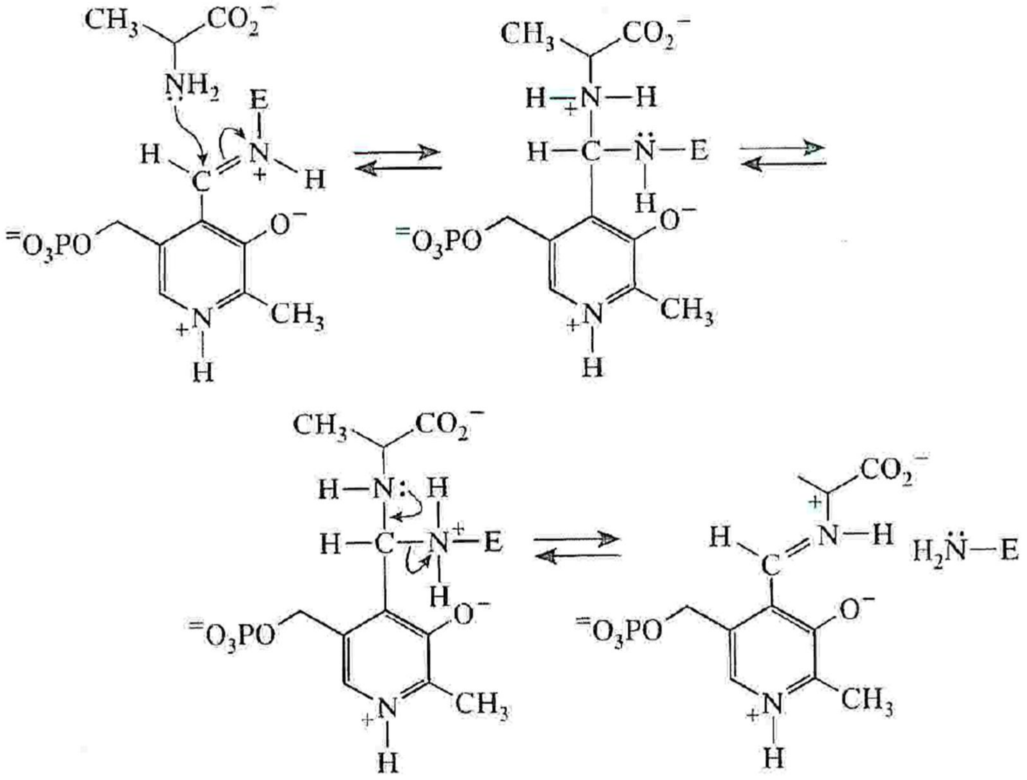


(b)



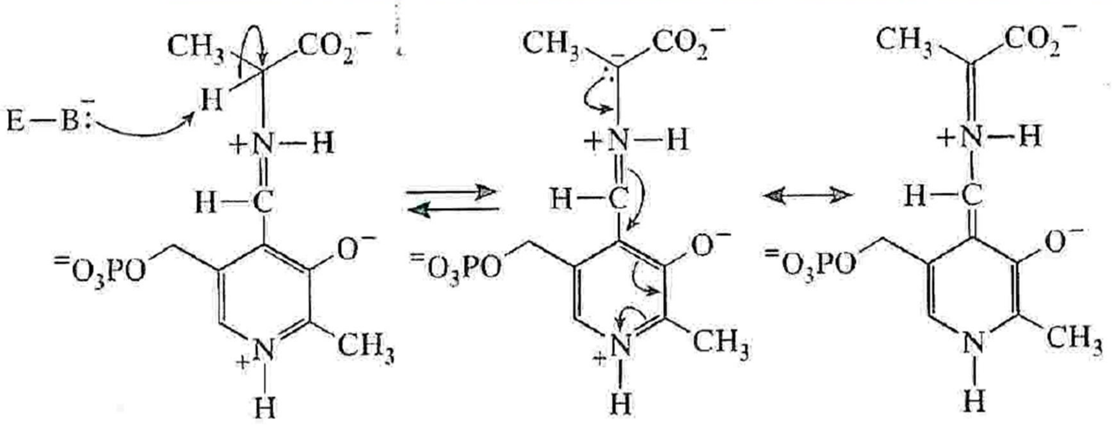
Problem 16.B1 ➤ Bir enzim bağlı PLP immininin, alanin gibi bir substrat bağlı PLP iminine nasıl dönüşebileceğini gösteren bir mekanizma yazınız.

16.B1



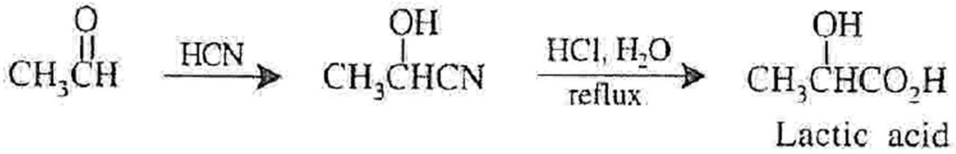
Problem 16.B2 ➤ Alaninin rasemleşmesinde α-karbanyonun, piridin halkasının konjugasyonuyla nasıl kararlı kılındığını gösteren rezonans yapılarını yazınız.

16.B2



Problem 16.16 ➤ (a) Asetaldehitten çıkarak, bir siyanohidrin ara ürünü üzerinden laktik asiti ($CH_3CHOHCO_2H$) nasıl hazırlayabileceğinizi gösteriniz. (b) Laktik asitin hangi stereoizomerini elde etmeyi umuyorsunuz?

16.16 (a)



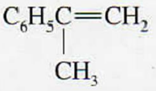
$$CH_3\overset{O}{\overset{\|}{C}}H \xrightarrow{HCN} CH_3\overset{OH}{\overset{|}{C}}HCN \xrightarrow[\text{reflux}]{HCl,\ H_2O} CH_3\overset{OH}{\overset{|}{C}}HCO_2H$$

Lactic acid

(b) A racemic form

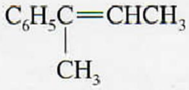
Problem 16.17 ➤ Başlangıç maddeleri olarak trifenilfosfine ek olarak gerekli aldehitlere, ketonlara ve organik halojenürlere sahip olduğunu varsayınız. Wittig tepkimesini kullanarak aşağıdaki her bir alkeni nasıl sentezleyebileceğiniz gösteriniz.

(a)



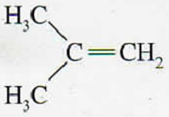
$$C_6H_5\underset{CH_3}{\underset{|}{C}}{=}CH_2$$

(b)

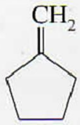


$$C_6H_5\underset{CH_3}{\underset{|}{C}}{=}CHCH_3$$

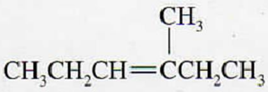
(c)



(d)



(e)

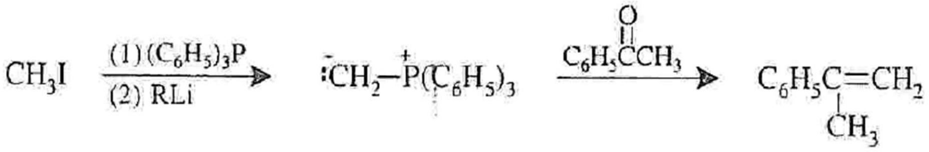


$$CH_3CH_2CH{=}\overset{CH_3}{\overset{|}{C}}CH_2CH_3$$

(f) $C_6H_5CH{=}CHCH{=}CH_2$

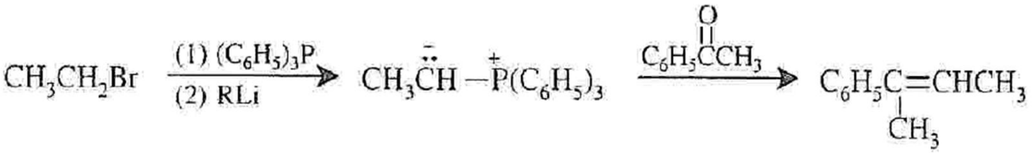
(g) $C_6H_5CH{=}CHC_6H_5$

16.17 (a)



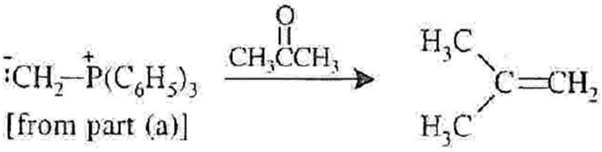
$$CH_3I \xrightarrow[(2)\ RLi]{(1)\ (C_6H_5)_3P} {:}\overset{-}{C}H_2-\overset{+}{P}(C_6H_5)_3 \xrightarrow{C_6H_5\overset{O}{\overset{\|}{C}}CH_3} C_6H_5\underset{\underset{CH_3}{|}}{C}{=}CH_2$$

(b)



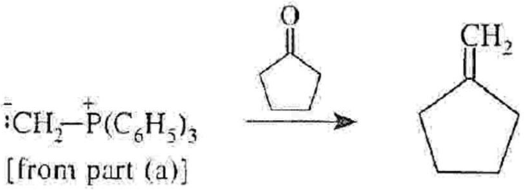
$$CH_3CH_2Br \xrightarrow[(2)\ RLi]{(1)\ (C_6H_5)_3P} CH_3\overset{\cdot\cdot}{\overset{-}{C}}H-\overset{+}{P}(C_6H_5)_3 \xrightarrow{C_6H_5\overset{O}{\overset{\|}{C}}CH_3} C_6H_5\underset{\underset{CH_3}{|}}{C}{=}CHCH_3$$

(c)

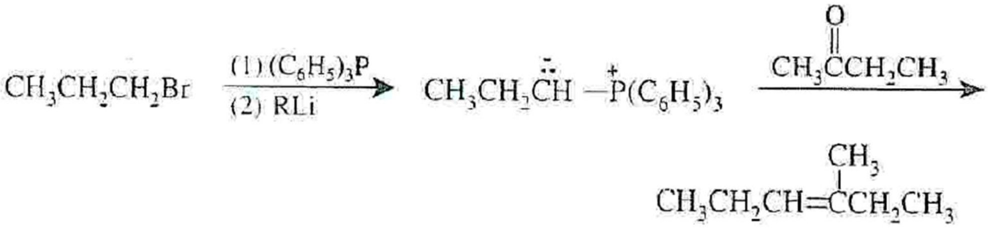


$:\overset{-}{C}H_2-\overset{+}{P}(C_6H_5)_3$
[from part (a)]
$CH_3\overset{O}{\overset{\|}{C}}CH_3$
H_3C
$C{=}CH_2$
H_3C

(d)

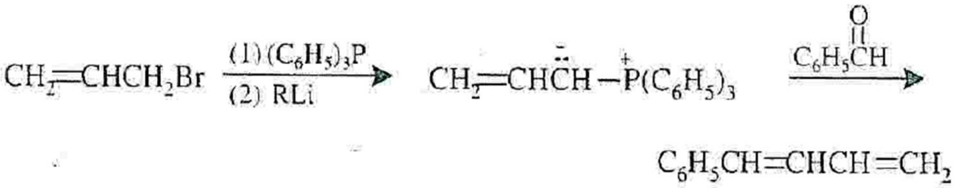


(e)



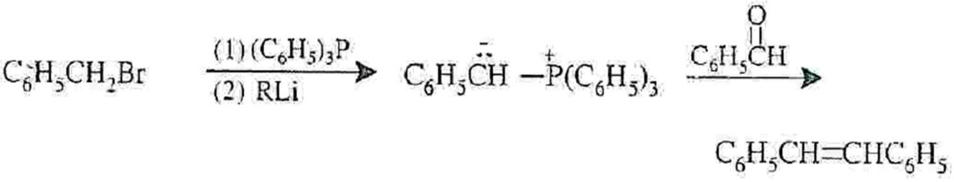
$$CH_3CH_2CH_2Br \xrightarrow[(2)\ RLi]{(1)\ (C_6H_5)_3P} CH_3CH_2\overset{\cdot\cdot}{\overset{-}{C}}H-\overset{+}{P}(C_6H_5)_3 \xrightarrow{CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3} CH_3CH_2CH{=}\overset{\overset{CH_3}{|}}{C}CH_2CH_3$$

(f)



$$CH_2{=}CHCH_2Br \xrightarrow[(2)\ RLi]{(1)\ (C_6H_5)_3P} CH_2{=}CH\overset{\cdot\cdot}{\overset{-}{C}}H-\overset{+}{P}(C_6H_5)_3 \xrightarrow{C_6H_5\overset{O}{\overset{\|}{C}}H} C_6H_5CH{=}CHCH{=}CH_2$$

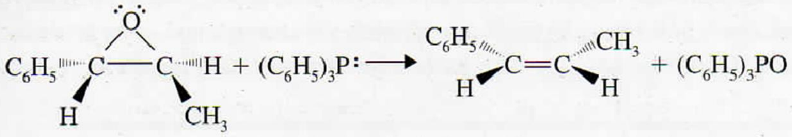
(g)



$$C_6H_5CH_2Br \xrightarrow[(2)\ RLi]{(1)\ (C_6H_5)_3P} C_6H_5\overset{\cdot\cdot}{\overset{-}{C}}H-\overset{+}{P}(C_6H_5)_3 \xrightarrow{C_6H_5\overset{O}{\overset{\|}{C}}H} C_6H_5CH{=}CHC_6H_5$$

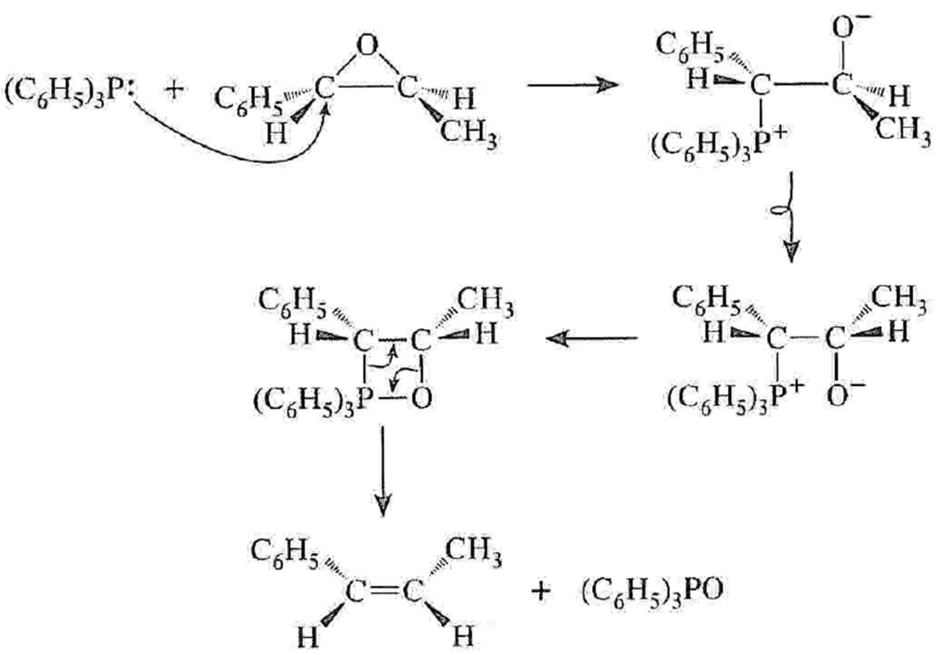
Problem 16.18

Trifenifosfin, epoksitlerin alkene dönüştürülmesinde de kullanabilir, örneğin;



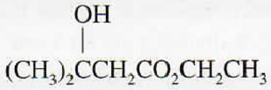
Bu tepkime için uygun bir mekanizma öneriniz.

16.18



Problem 16.19 ➤ Aşağıdaki bileşiklerin her birinin sentezinde Reformatsky tepkimesini nasıl kullanabileceğinizi gösteriniz. (Bazı durumlarda ek basamaklar gerekebilir.)

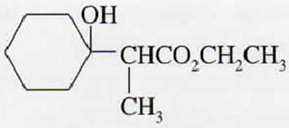
(a)



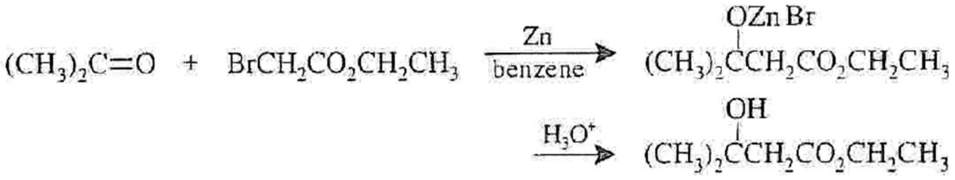
$(CH_3)_2\overset{OH}{\overset{|}{C}}CH_2CO_2CH_2CH_3$

(c) $CH_3CH_2CH_2CH_2CO_2CH_2CH_3$

(b)

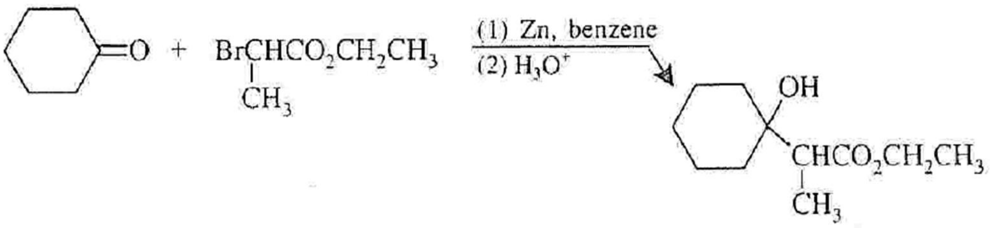


16.19 (a)

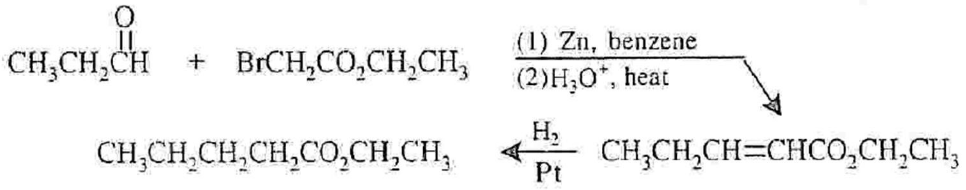


$$(CH_3)_2C{=}O + BrCH_2CO_2CH_2CH_3 \xrightarrow[\text{benzene}]{\text{Zn}} (CH_3)_2\overset{OZnBr}{\overset{|}{C}}CH_2CO_2CH_2CH_3 \xrightarrow{H_3O^+} (CH_3)_2\overset{OH}{\overset{|}{C}}CH_2CO_2CH_2CH_3$$

(b)



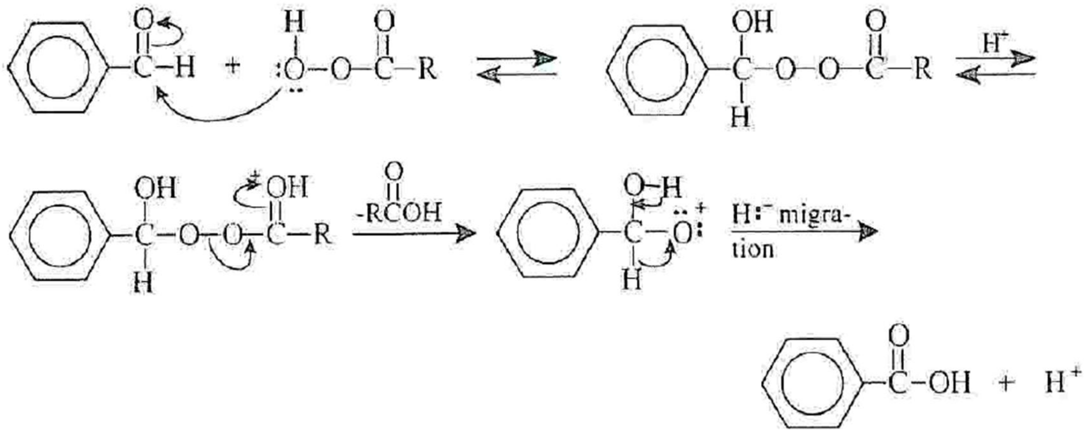
(c)



$$CH_3CH_2\overset{O}{\overset{||}{C}}H + BrCH_2CO_2CH_2CH_3 \xrightarrow[\text{(2) }H_3O^+\text{, heat}]{\text{(1) Zn, benzene}} CH_3CH_2CH{=}CHCO_2CH_2CH_3 \xrightarrow[\text{Pt}]{H_2} CH_3CH_2CH_2CH_2CO_2CH_2CH_3$$

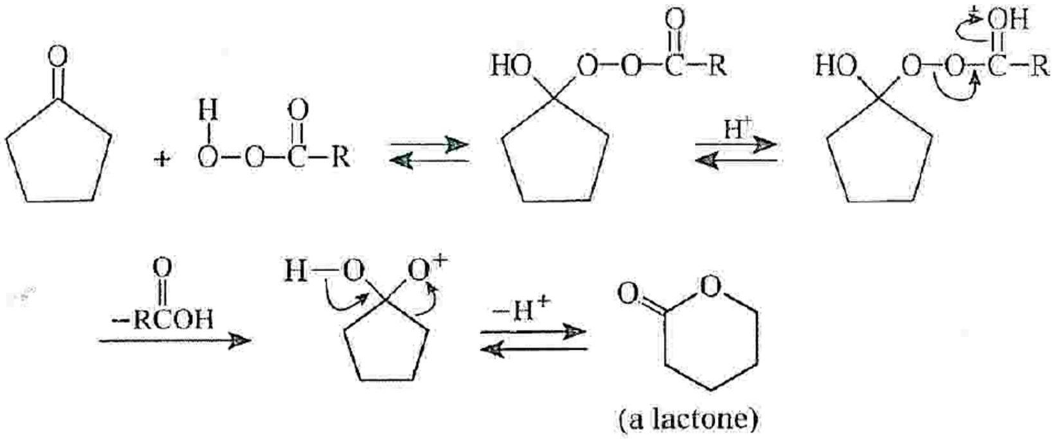
Problem 16.20 ➤ Benzaldehit bir peroksiasit ile tepkimeye girdiğinde ürün benzoik asittir. Bu tepkimenin mekanizması asetofenon için az önce verilenin benzeridir ve sonuç, fenile göre hidrojen atomunun daha büyük göçme kabiliyeti olduğunu gösterir. Söz konusu tüm basamakları gösteriniz.

16.20



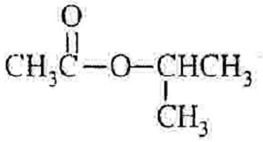
Problem 16.21 ➤ Siklopentanonun Baeyer-Villiger yükseltgenmesinden oluşabilecek ürünün yapısını yazınız.

16.21 The product is a lactone, formed as follows:



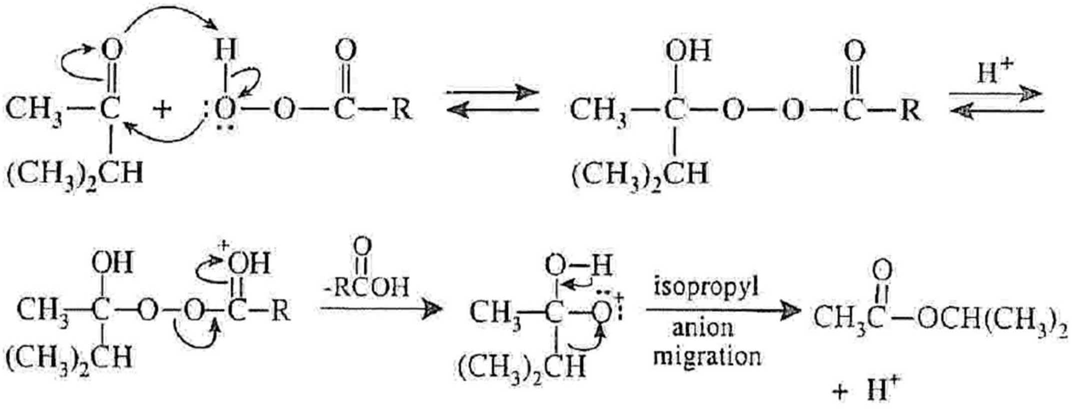
Problem 16.22 ➤ 3-Metil-2-bütanonun Bayer-Villiger yükseltgenmesinden oluşabilecek ana ürün nedir?

16.22



$CH_3C(=O)-O-CH(CH_3)CH_3$

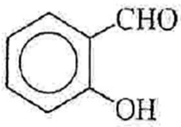
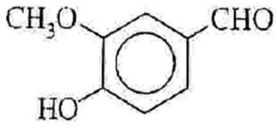
The isopropyl group has a greater migratory aptitude than the methyl group. The mechanism is as follows:



16.23 Aşağıdaki bileşiklerin her biri için bir yapı formülü yazınız ve bir başka kabul edilebilir isim veriniz.

(a) Formaldehit
(b) Asetaldehit
(c) Fenilasetaldehit
(d) Aseton
(e) Etil metil keton
(f) Asetofenon
(g) Benzofenon
(h) Salisilaldehit
(i) Vanilin
(j) Dietil keton
(k) Etil izopropil keton
(l) Diizopropil keton
(m) Dibütil keton
(n) Dipropil keton
(o) Sinnamaldehit

16.23

(a)	$HCHO$	Methanal
(b)	CH_3CHO	Ethanal
(c)	$C_6H_5CH_2CHO$	Phenylethanal
(d)	CH_3COCH_3	Propanone
(e)	$CH_3COCH_2CH_3$	Butanone
(f)	$CH_3COC_6H_5$	1-Phenylethanone or methyl phenyl ketone
(g)	$C_6H_5COC_6H_5$	Diphenylmethanone or diphenyl ketone
(h)		2-Hydroxybenzaldehyde or *o*-hydroxybenzaldehyde
(i)		4-Hydroxy-3-methoxybenzaldehyde
(j)	$CH_3CH_2COCH_2CH_3$	3-Pentanone
(k)	$CH_3CH_2COCH(CH_3)_2$	2-Methyl-3-pentanone
(l)	$(CH_3)_2CHCOCH(CH_3)_2$	2,4-Dimethyl-3-pentanone
(m)	$CH_3(CH_2)_3CO(CH_2)_3CH_3$	5-Nonanone
(n)	$CH_3(CH_2)_2CO(CH_2)_2CH_3$	4-Heptanone
(o)	$C_6H_5CH{=}CHCHO$	3-Phenyl-2-propenal

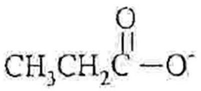
16.24 Propanol, aşağıdaki her bir reaktifle tepkimeye girdiğinde oluşacak ürünlerin yapı formüllerini yazınız.

(a) $NaBH_4$, sulu NaOH içerisinde
(b) C_6H_5MgBr, sonra H_2O
(c) $LiA1H_4$, sonra H_2O
(d) Ag_2O, OH^-
(e) $(C_6H_5)_3P{=}CH_2$
(f) H_2 ve Pt
(g) $HOCH_2CH_2OH$ ve HA
(h) $CH_3\overset{-}{\ddot{C}}H — \overset{+}{P}(C_6H_5)_3$
(i) (1) $BrCH_2CO_2C_2H_5$, Zn; (2) H_3O^+
(j) $Ag(NH_3)_2^+$
(k) Hidroksilamin
(l) Semikarbazit
(m) Fenilhidrazin
(n) Soğuk seyreltik $KMnO_4$
(o) $HSCH_2CH_2SH$, HA
(p) $HSCH_2CH_2SH$, HA, sonra Raney nikeli

16.24 (a) $CH_3CH_2CH_2OH$

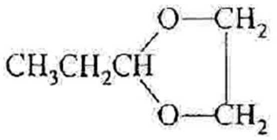
(b) $CH_3CH_2CHOHC_6H_5$

(c) $CH_3CH_2CH_2OH$

(d) 
$CH_3CH_2\overset{O}{\overset{\|}{C}}-O^-$

(e) $CH_3CH_2CH{=}CH_2$

(f) $CH_3CH_2CH_2OH$

(g) 

(h) $CH_3CH_2CH{=}CHCH_3$

(i) $CH_3CH_2CHOHCH_2CO_2C_2H_5$

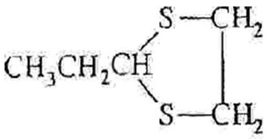
(j) $CH_3CH_2CO_2^- NH_4^+ + Ag\downarrow$

(k) $CH_3CH_2CH{=}NOH$

(l) $CH_3CH_2CH{=}NNHCONH_2$

(m) $CH_3CH_2CH{=}NNHC_6H_5$

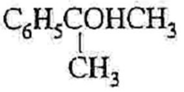
(n) $CH_3CH_2CO_2H$

(o) 

(p) $CH_3CH_2CH_3 + CH_3CH_3 + NiS$

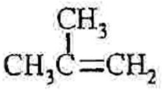
16.25 Asetonun, Problem 16.24'teki her bir reaktifle tepkimesinden oluşan (eğer oluşursa) ürünlerin yapı formüllerini yazınız.

16.25 (a) $CH_3CHOHCH_3$

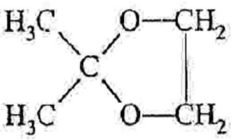
(b) 
$C_6H_5\underset{CH_3}{\underset{|}{C}}OHCH_3$

(c) $CH_3CHOHCH_3$

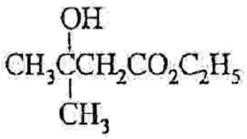
(d) No reaction

(e) 
$CH_3\overset{CH_3}{\overset{|}{C}}{=}CH_2$

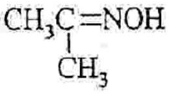
(f) $CH_3CHOHCH_3$

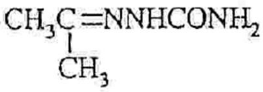
(g) 

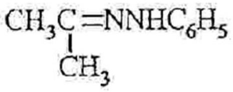
(h) $CH_3CH{=}C(CH_3)_2$

(i) 
$CH_3\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}CH_2CO_2C_2H_5$

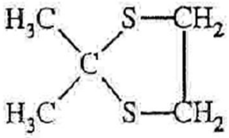
(j) No reaction

(k) 
$CH_3\underset{CH_3}{\underset{|}{C}}{=}NOH$

(l) 
$CH_3\underset{CH_3}{\underset{|}{C}}{=}NNHCONH_2$

(m) 
$CH_3\underset{CH_3}{\underset{|}{C}}{=}NNHC_6H_5$

(n) No reaction

(o) 

(p) $CH_3CH_2CH_3 + CH_3CH_3 + NiS$

16.26 Asetofenonun aşağıdaki tepkimelerinin her birinden ne elde ederdiniz?

(a) Asetofenon $+$ $HNO_3 \xrightarrow[H_2SO_4]{}$

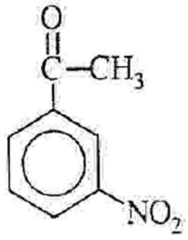
(b) Asetofenon $+$ $C_6H_5NHNH_2 \longrightarrow$

(c) Asetofenon $+$ $\overset{-}{:C}H_2-\overset{+}{P}(C_6H_5)_3 \longrightarrow$

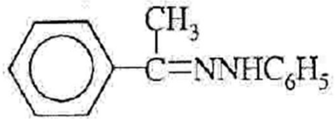
(d) Asetofenon $+$ $NaBH_4 \xrightarrow[OH^-]{H_2O}$

(e) Asetofenon $+$ $C_6H_5MgBr \xrightarrow[(2)\ H_2O]{}$

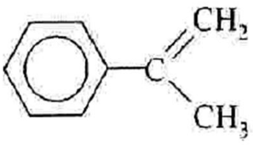
16.26 (a)



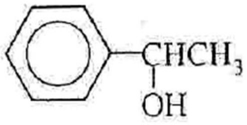
(b)



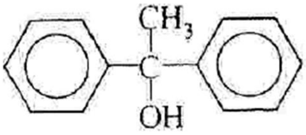
(c)



(d)

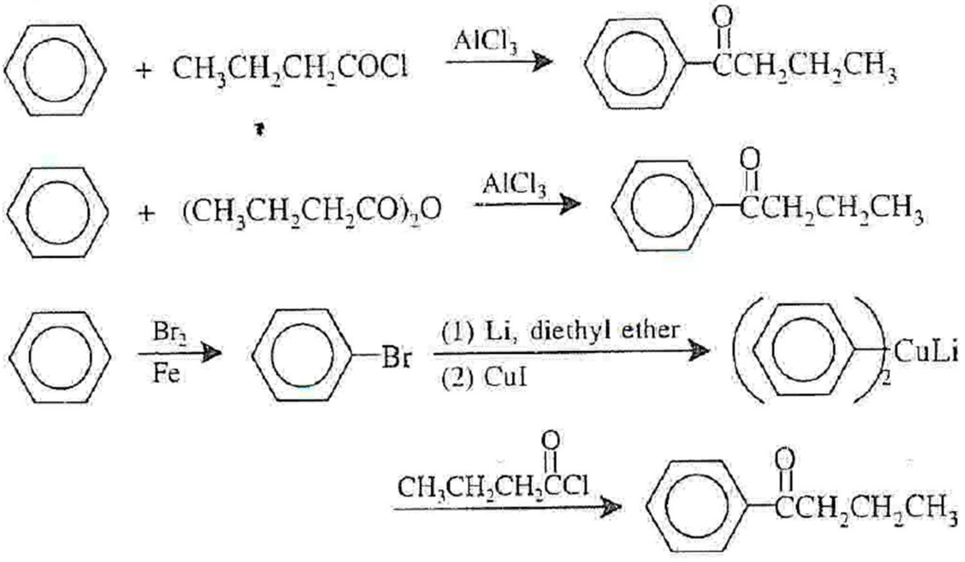


(e)

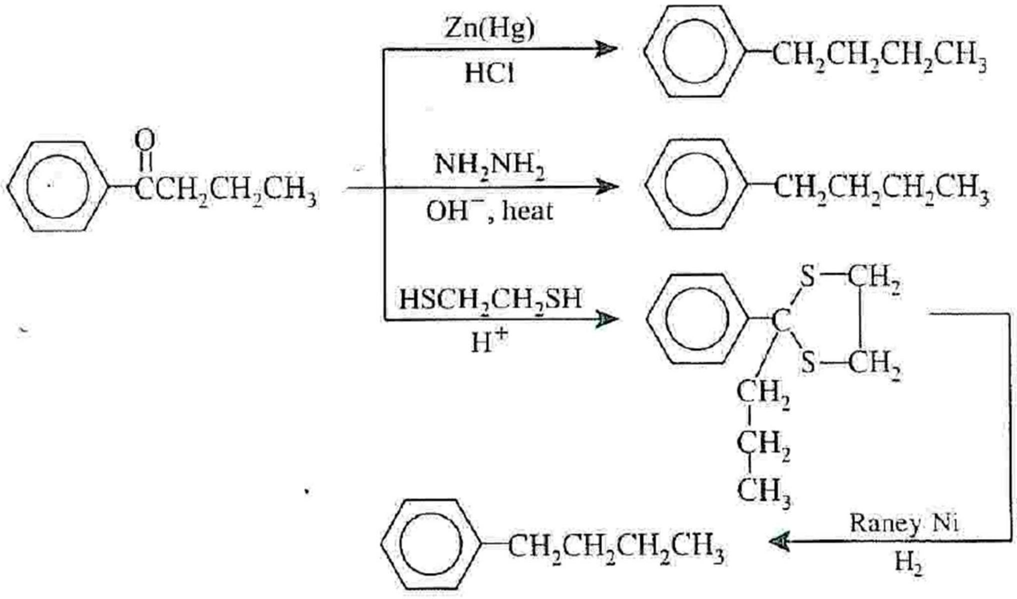


16.27 (**a**) Fenil propil ketonun benzen ve gerekli olan diğer reaktiflerden sentezi için üç yöntem öneriniz. (**b**) Fenil propil ketonun bütilbenzene dönüşümü için de üç yöntem belirtiniz.

16.27 (a)



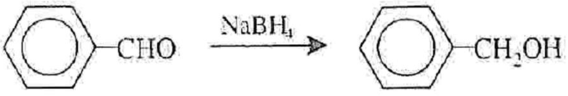
(b)



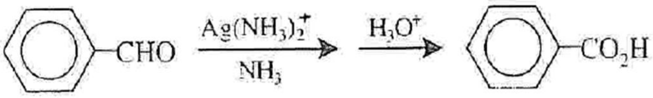
16.28 Benzaldehiti aşağıdaki her bir bileşiğe nasıl dönüştürebileceğinizi gösteriniz. Gerek duyulan herhangi bir reaktif kullanabilir ve birden fazla basamağa ihtiyaç duyabilirsiniz.

- **(a)** Benzil alkol
- **(b)** Benzoik asit
- **(c)** Benzoil klorür
- **(d)** Benzofenon
- **(e)** Asetofenon
- **(f)** 1-Feniletanol
- **(g)** 3-Metil-1-fenil-1-bütanol
- **(h)** Benzil bromür
- **(i)** Toluen
- **(j)** $C_6H_5CH(OCH_3)_2$
- **(k)** $C_6H_5CH^{18}O$
- **(l)** C_6H_5CHDOH
- **(m)** $C_6H_5CH(OH)CN$
- **(n)** $C_6H_5CH{=}NOH$
- **(o)** $C_6H_5CH{=}NNHC_6H_5$
- **(p)** $C_6H_5CH{=}NNHCONH_2$
- **(q)** $C_6H_5CH{=}CHCH{=}CH_2$

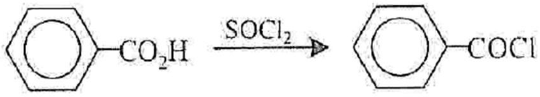
16.28 (a)



(b)

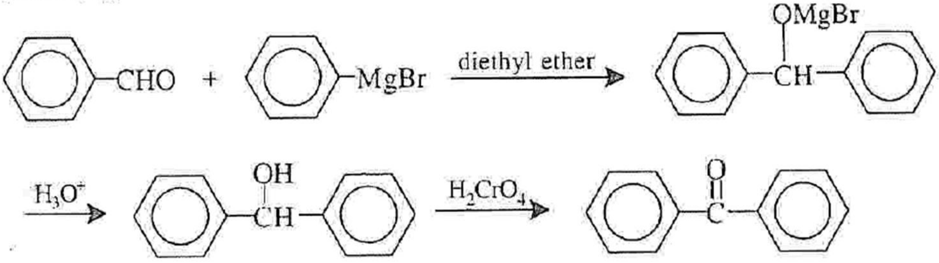


(c)

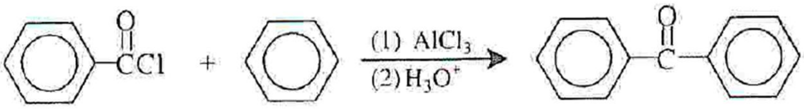


[from (b)]

(d)

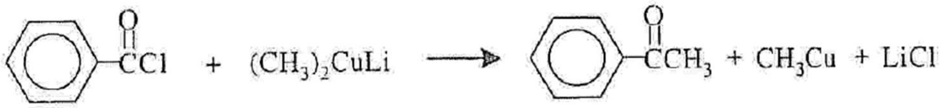


or



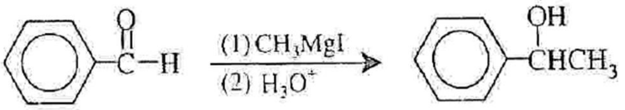
[from (c)]

(e)

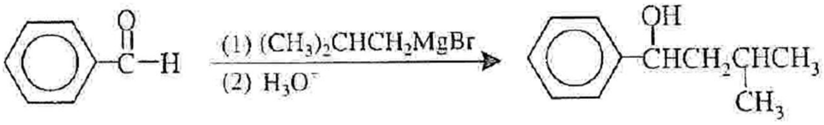


[from (c)]

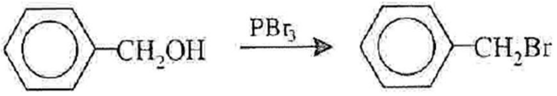
(f)



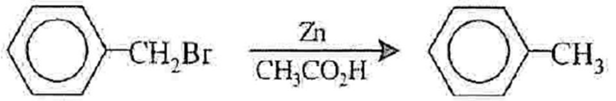
(g)



(h)

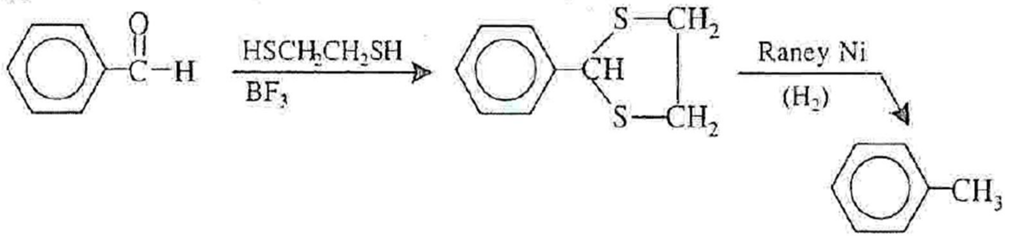


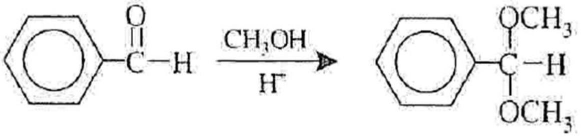
[from (a)]

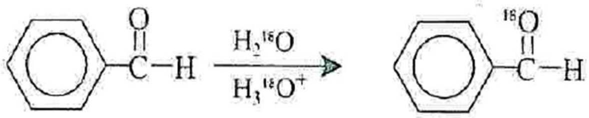
(i) 

[from (h)]

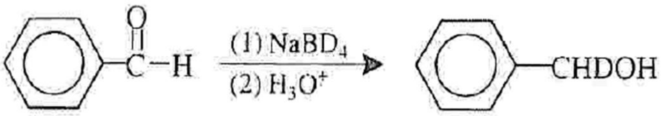
or

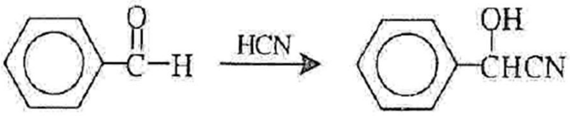


(j) 

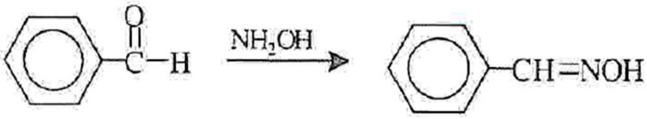
(k) 

(See problem 16.8 for the mechanism)

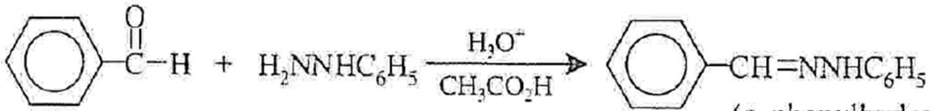
(l) 

(m) 

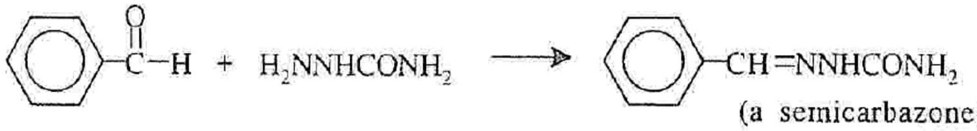
(a cyanohydrin)

(n) 

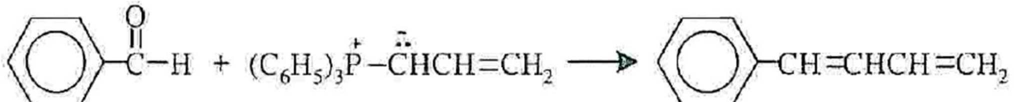
(an oxime)

(o) 

(a phenylhydrazone)

(p) 

(a semicarbazone)

(q) 

(a Wittig reagent)

16.29 Etil fenil ketonun aşağıdaki bileşiklerin her birinden nasıl sentezlenebileceğini gösteriniz:

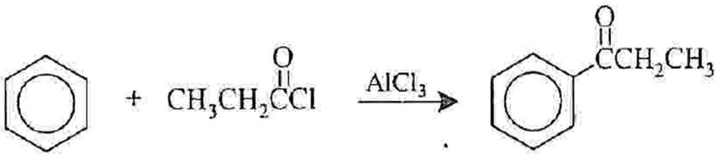
(a) Benzen

(b) Benzol klorür

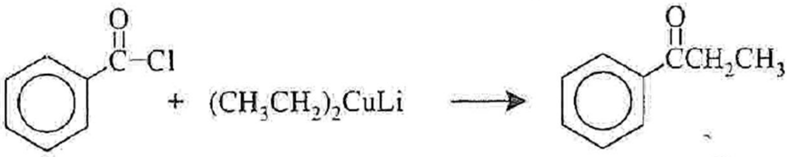
(c) Benzonitril, C_6H_5CN

(d) Benzaldehit

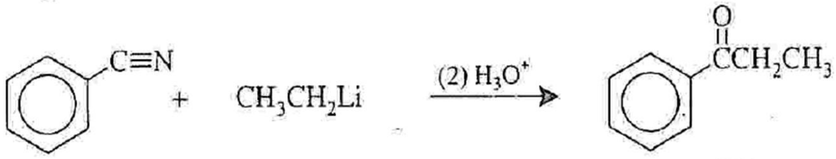
16.29 (a)



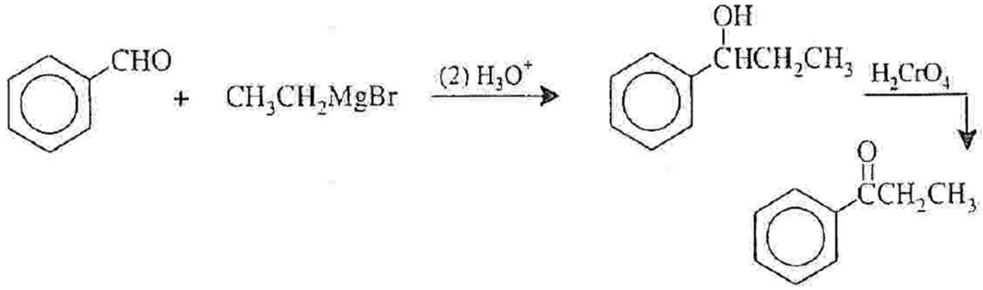
(b)



(c)



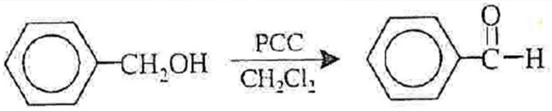
(d)



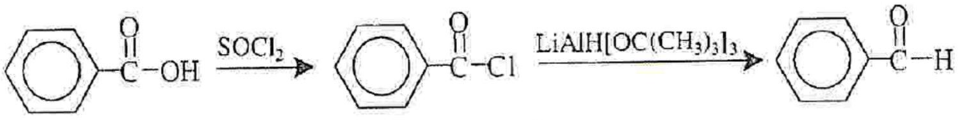
16.30 Benzaldehitin aşağıdaki bileşiklerin her birinden nasıl sentezlenebileceğini gösteriniz.

(a) Benzil alkol	**(c)** Feniletin,	**(e)** $C_6H_5CO_2CH_3$
(b) Benzoik asit	**(d)** Fenileten (stiren)	**(f)** $C_6H_5C{\equiv}N$

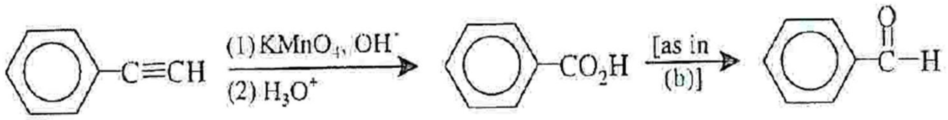
16.30 (a)



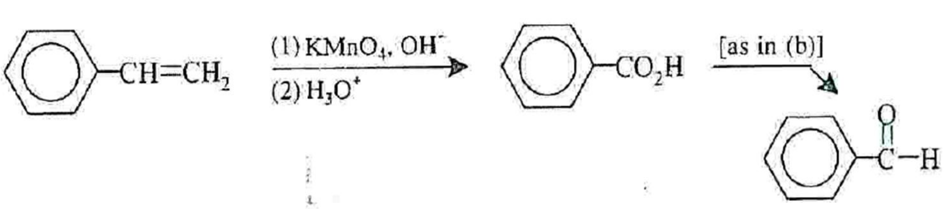
(b)



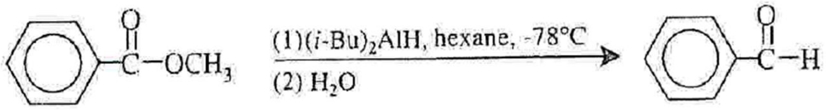
(c)



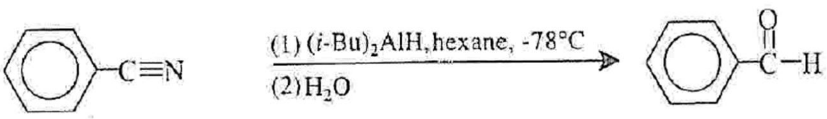
(d)



(e)



(f)

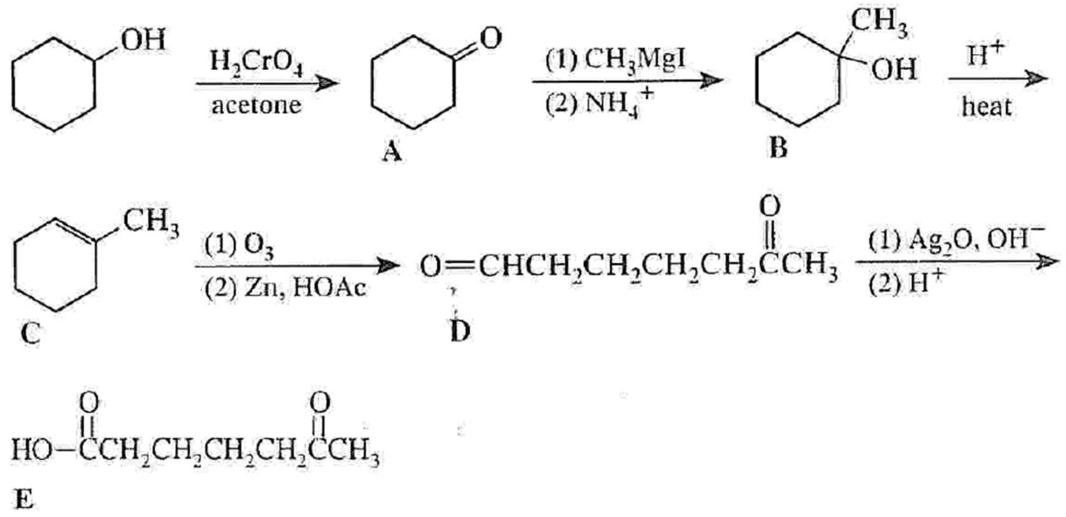


16.31 **A – E** bileşiklerinin yapılarını yazınız.

$$\text{Sikloheksanol} \xrightarrow[\text{aseton}]{H_2CrO_4} \mathbf{A}\ (C_6H_{10}O) \xrightarrow[(2)\ H_3O^+]{(1)\ CH_3MgI} \mathbf{B}\ (C_7H_{14}O) \xrightarrow[\text{ısı}]{HA}$$

$$\mathbf{C}\ (C_7H_{12}) \xrightarrow[(2)\ Zn,\ HOAc]{(1)\ O_3} \mathbf{D}\ (C_7H_{12}O_2) \xrightarrow[(2)\ H_3O^-]{(1)\ Ag_2O,\ OH^-} \mathbf{E}\ (C_7H_{12}O_3)$$

16.31

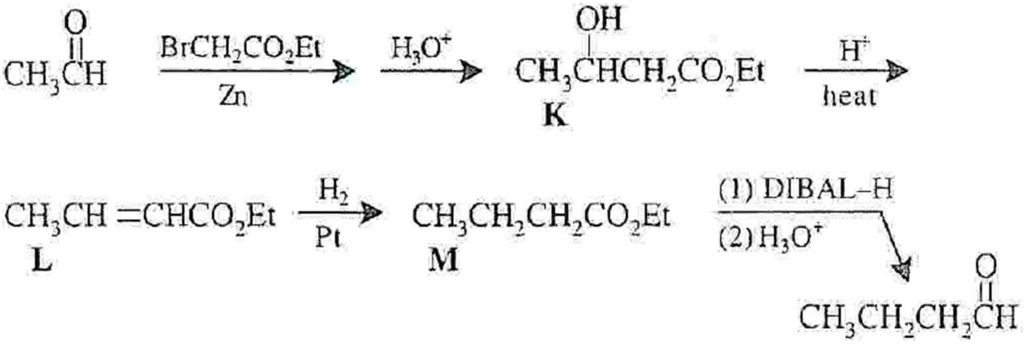


16.32 Aşağıdaki tepkime dizisi, bir aldehitin karbon zincirinin iki karbon atomu daha nasıl uzatılabileceğini gösteriyor. **K – M** ara ürünlerinin yapıları nasıldır?

$$\text{Etanal} \xrightarrow[(2)\ H_3O^+]{(1)\ BrCH_2CO_2Et,\ Zn} \mathbf{K}\ (C_6H_{12}O_3) \xrightarrow{HA,\ \text{ısı}}$$

$$\mathbf{L}\ (C_6H_{10}O_2) \xrightarrow{H_2,\ Pt} \mathbf{M}\ (C_6H_{12}O_2) \xrightarrow[(2)\ H_2O]{(1)\ DIBAL\text{-}H} \text{bütanal}$$

16.32

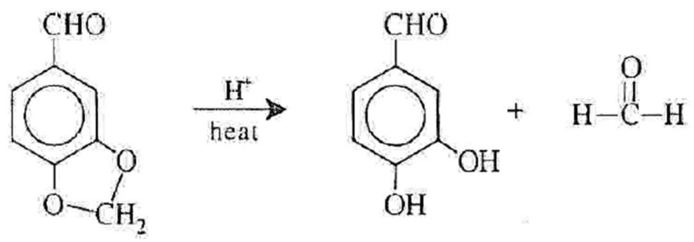


$$CH_3\overset{O}{\overset{\|}{C}}H \xrightarrow[Zn]{BrCH_2CO_2Et} \xrightarrow{H_3O^+} \underset{\mathbf{K}}{CH_3\overset{OH}{\overset{|}{C}}HCH_2CO_2Et} \xrightarrow[\text{heat}]{H^+}$$

$$\underset{\mathbf{L}}{CH_3CH{=}CHCO_2Et} \xrightarrow[Pt]{H_2} \underset{\mathbf{M}}{CH_3CH_2CH_2CO_2Et} \xrightarrow[(2)\ H_3O^+]{(1)\ DIBAL\text{-}H} CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}H$$

16.33 Seyreltik HC1 ile ısıtılması, piperonali (Altbölüm 16.3) $C_7H_6O_3$ formülüne sahip bir bileşiğe çevirir. Bu bileşik nedir ve ne tür bir tepkime olmuştur?

16.33



The compound $C_7H_6O_3$ is 3,4-dihydroxybenzaldehyde. The reaction involves hydrolysis of the acetal of formaldehyde.

16.34 Benzil bromürden başlayarak, aşağıdaki her bir bileşiği nasıl sentezleyeceğinizi gösteriniz.

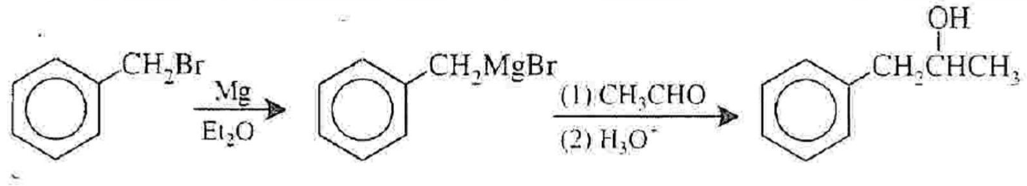
(a) $C_6H_5CH_2CHOHCH_3$

(b) $C_6H_5CH_2CH_2CHO$

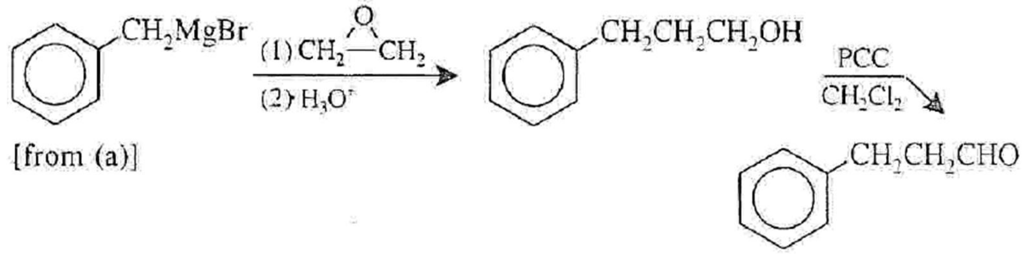
(c) $C_6H_5CH{=}CH{-}CH{=}CHC_6H_5$

(d) $C_6H_5CH_2COCH_2CH_3$

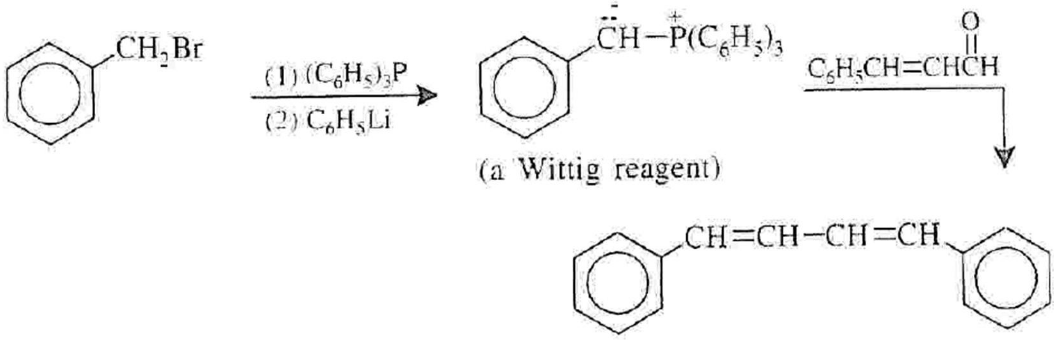
16.34 (a)



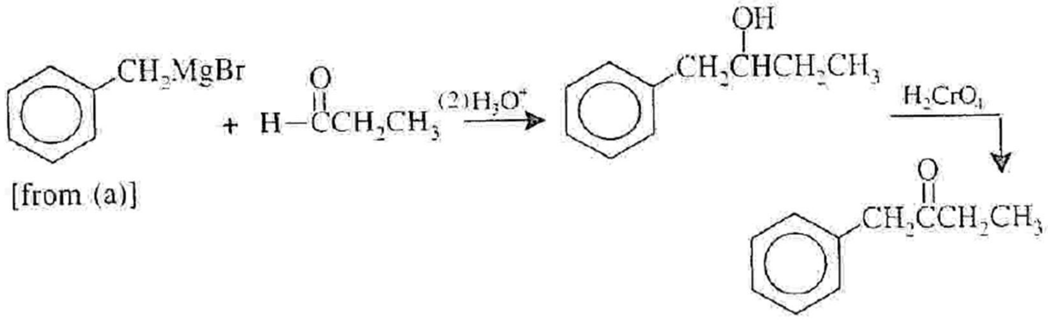
(b)



(c)



(d)

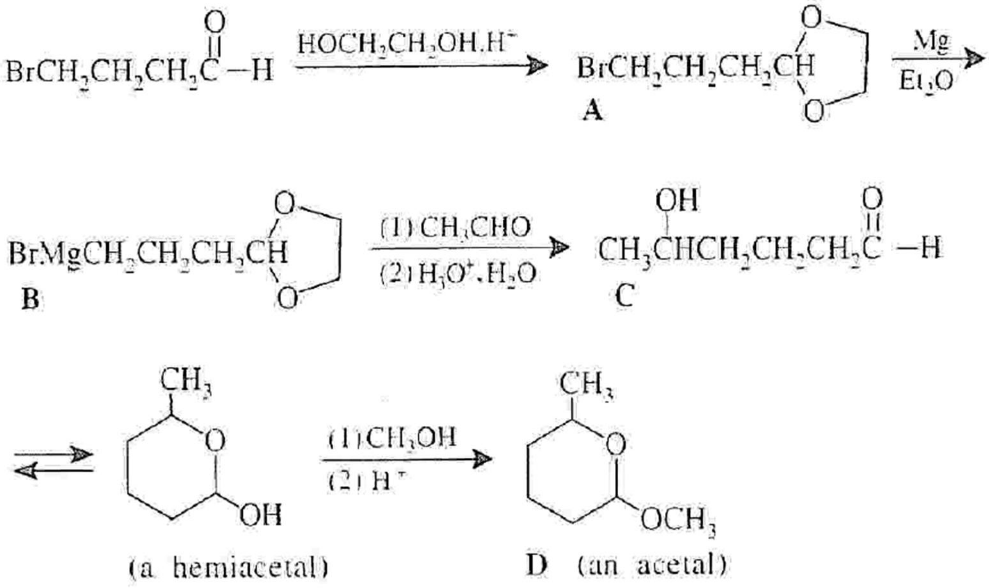


16.35 **A** ve **D** Bileşikleri olumlu Tollens testi vermemesine karşın, **C** bileşiği olumlu test verir. **A – D**'nin yapılarını yazınız.

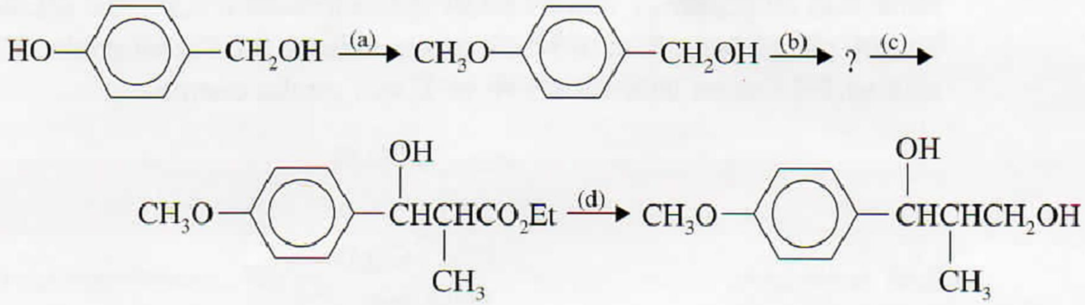
$$\text{4-Bromobütanal} \xrightarrow{HOCH_2CH_2OH,\ HA} \mathbf{A}\ (C_6H_{11}O_2Br) \xrightarrow{Mg,\ Et_2O}$$

$$[\mathbf{B}\ (C_6H_{11}MgO_2Br)] \xrightarrow[(2)\ H_3O^+,\ H_2O]{(1)\ CH_3CHO} \mathbf{C}\ (C_6H_{12}O_2) \xrightarrow[HA]{CH_3OH} \mathbf{D}\ (C_7H_{14}O_2)$$

16.35



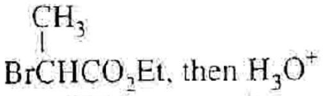
16.36 Aşağıdaki sentezde gösterilmeyen reaktifleri ve ara ürünleri belirtiniz.



16.36 (a) $(CH_3)_2SO_4$, NaOH, or CH_3I, NaOH

(b) PCC/CH_2Cl_2

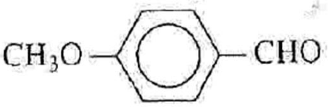
(c) Zn,



$\overset{\displaystyle CH_3}{BrCHCO_2Et}$, then H_3O^+

(d) $LiAlH_4$, then H_2O

Intermediate is

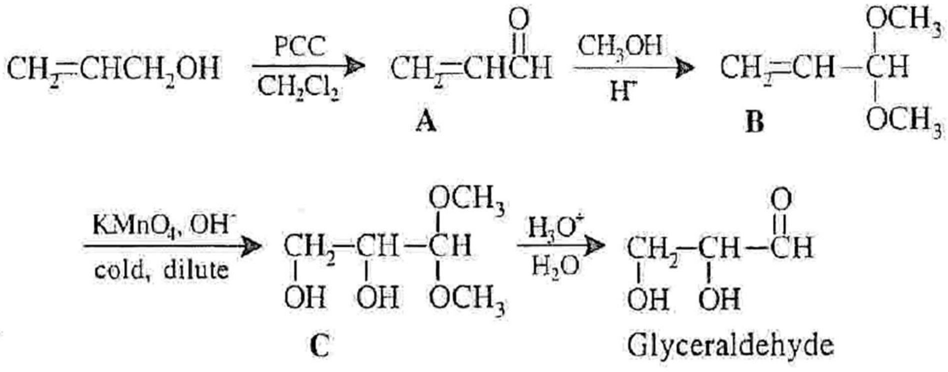


16.37 Gliseraldehitin (Altbölüm 5.14A) bir sentezi burada gösterilmektedir. **A – C** ara ürünleri nelerdir ve gliseraldehitin hangi stereoizomerini elde edebileceğinizi umuyorsunuz?

$$CH_2{=}CHCH_2OH \xrightarrow[CH_2Cl_2]{PCC} \mathbf{A}\ (C_3H_4O) \xrightarrow{CH_3OH,\ HA}$$

$$\mathbf{B}\ (C_5H_{10}O_2) \xrightarrow[\text{soğuk, seyreltik}]{KMnO_4,\ OH^-} \mathbf{C}\ (C_5H_{12}O_4) \xrightarrow[H_2O]{H_3O^+} \text{gliseraldehit}$$

16.37



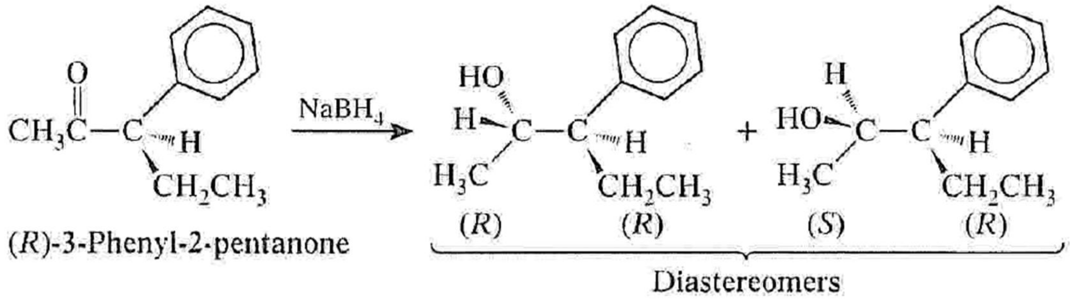
$$CH_2{=}CHCH_2OH \xrightarrow[CH_2Cl_2]{PCC} \underset{\textbf{A}}{CH_2{=}CH\overset{O}{\overset{\|}{C}}H} \xrightarrow[H^+]{CH_3OH} \underset{\textbf{B}}{CH_2{=}CH{-}\overset{OCH_3}{\overset{|}{\underset{\underset{OCH_3}{|}}{C}}}H}$$

$$\xrightarrow[\text{cold, dilute}]{KMnO_4,\ OH^-} \underset{\textbf{C}}{\underset{\underset{OH}{|}}{C}H_2{-}\underset{\underset{OH}{|}}{C}H{-}\overset{OCH_3}{\overset{|}{\underset{\underset{OCH_3}{|}}{C}}}H} \xrightarrow[H_2O]{H_3O^+} \underset{\text{Glyceraldehyde}}{\underset{\underset{OH}{|}}{C}H_2{-}\underset{\underset{OH}{|}}{C}H{-}\overset{O}{\overset{\|}{C}}H}$$

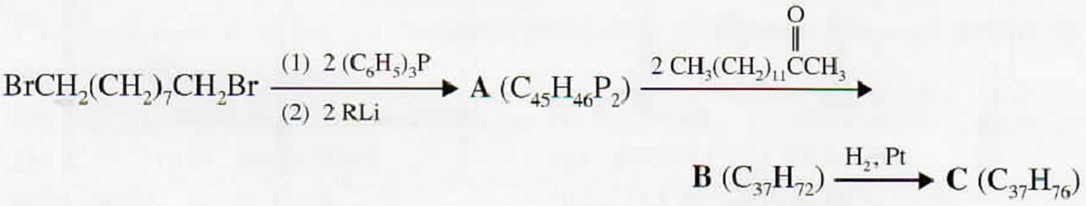
The product would be racemic as no chiral reagents were used.

16.38 (*R*)-3-Fenil-2-pentanonun sodyum borhidrür ile indirgenmesini göz önüne alınız. İndirgenme tamamlandıktan sonra, karışım kromatografi ile iki kısıma ayrılır. Bu kısımlar izomerik bileşikler içerir ve her izomer optikçe aktiftir. Bu iki izomer nedir ve bunlar arasındaki stereoizomerik ilişki nedir?

16.38



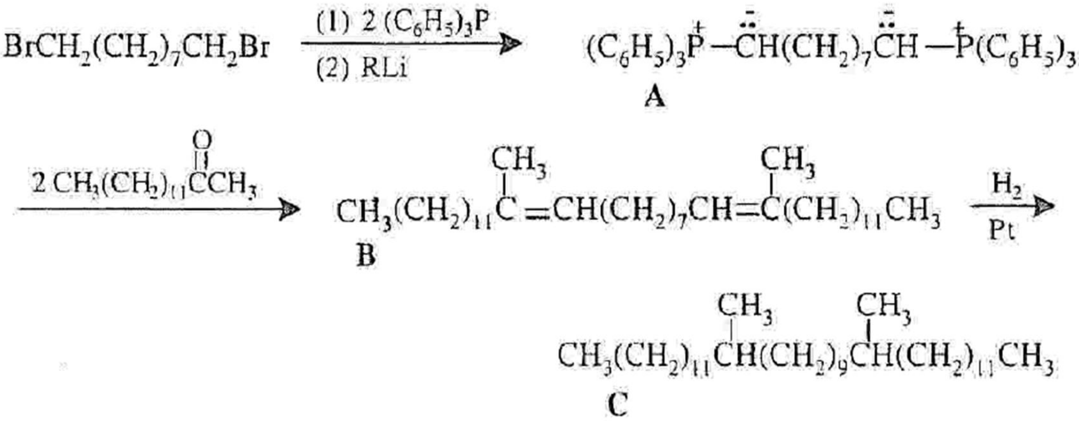
16.39 Uyku sineği dişisinin seks feromonunun (sekicisinin) yapısı aşağıdaki sentezle doğrulanmıştır. **C** bileşiğinin, doğal feromonun her yönden aynısı olduğu görülmüştür (erkek sineğin davranışı dahil). **A, B** ve **C** için yapılar öneriniz.



$$BrCH_2(CH_2)_7CH_2Br \xrightarrow[(2)\ 2\,RLi]{(1)\ 2\,(C_6H_5)_3P} \textbf{A}\ (C_{45}H_{46}P_2) \xrightarrow{2\,CH_3(CH_2)_{11}\overset{O}{\overset{\|}{C}}CH_3}$$

$$\textbf{B}\ (C_{37}H_{72}) \xrightarrow{H_2,\ Pt} \textbf{C}\ (C_{37}H_{76})$$

16.39



$$BrCH_2(CH_2)_7CH_2Br \xrightarrow[(2)\ RLi]{(1)\ 2\,(C_6H_5)_3P} \underset{\textbf{A}}{(C_6H_5)_3\overset{+}{P}{-}\overset{..}{\underset{-}{C}}H(CH_2)_7\overset{..}{\underset{-}{C}}H{-}\overset{+}{P}(C_6H_5)_3}$$

$$\xrightarrow{2\,CH_3(CH_2)_{11}\overset{O}{\overset{\|}{C}}CH_3} \underset{\textbf{B}}{CH_3(CH_2)_{11}\overset{CH_3}{\overset{|}{C}}{=}CH(CH_2)_7CH{=}\overset{CH_3}{\overset{|}{C}}(CH_2)_{11}CH_3} \xrightarrow[Pt]{H_2}$$

$$\underset{\textbf{C}}{CH_3(CH_2)_{11}\overset{CH_3}{\overset{|}{C}}H(CH_2)_9\overset{CH_3}{\overset{|}{C}}H(CH_2)_{11}CH_3}$$

16.40 Aşağıdaki her bir şık için, bileşikleri birbirinden ayırt edici basit kimyasal testler öneriniz.

(a) Benzaldehit ve benzil alkol

(b) Heksanal ve 2-heksanon

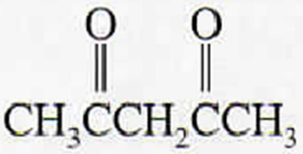
(c) 2-Heksanon ve heksan

(d) 2-Heksanol ve 2-heksanon

(e) $C_6H_5CH{=}CHCOC_6H_5$ ve $C_6H_5COC_6H_5$

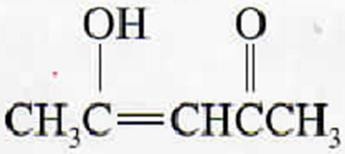
(f) Pentanal ve dietil eter

(g)



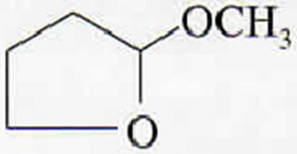
$CH_3\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{O}{\|}}{C}CH_3$

ve

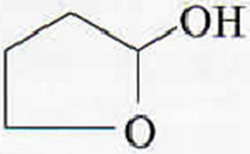


$CH_3\overset{\overset{OH}{|}}{C}{=}CH\overset{\overset{O}{\|}}{C}CH_3$

(h)



ve



16.40 (a) $Ag(NH_3)_2{}^+OH^-$ (positive test with benzaldehyde)

(b) $Ag(NH_3)_2{}^+OH^-$ (positive test with hexanal)

(c) Concentrated H_2SO_4 (2-hexanone is soluble)

(d) CrO_3 in H_2SO_4 (positive test with 2-hexanol)

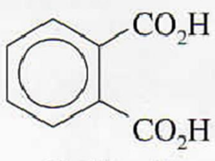
(e) Br_2 in CCl_4 (decolorization with $C_6H_5CH{=}CHCOC_6H_5$)

(f) $Ag(NH_3)_2{}^+OH^-$ (positive test with pentanal)

(g) Br_2 in CCl_4 (immediate decolorization occurs with enol form)

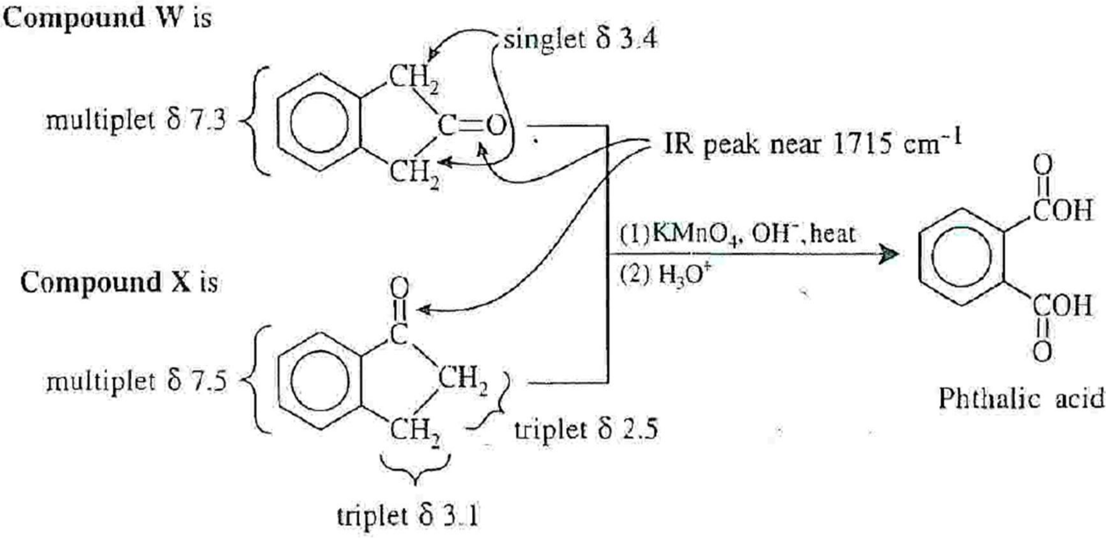
(h) $Ag(NH_3)_2{}^+OH^-$ (positive test with cyclic hemiacetal)

16.41 **W** ve **X** bileşikleri izomerlerdir ve C_9H_8O molekül formüllerine sahiplerdir. Her biri 1715 cm^{-1} civarında kuvvetli bir soğurma bandı verir. Her birinin sıcak, bazik potasyum permanganat ile yükseltgenmesi ve ardından asitlendirilmesi ftalik asiti oluşturur. **W**'nun ^{1}H NMR spektrumunda δ 7,3'te bir çoklu, δ 3,4'te bir birli pik görünür. **X**'in ^{1}H NMR spektrumda ise δ 7,5'te bir çoklu, δ 3,1'de bir üçlü ve δ 2,5'te bir üçlü vardır. **W** ve **X** için yapılar öneriniz.

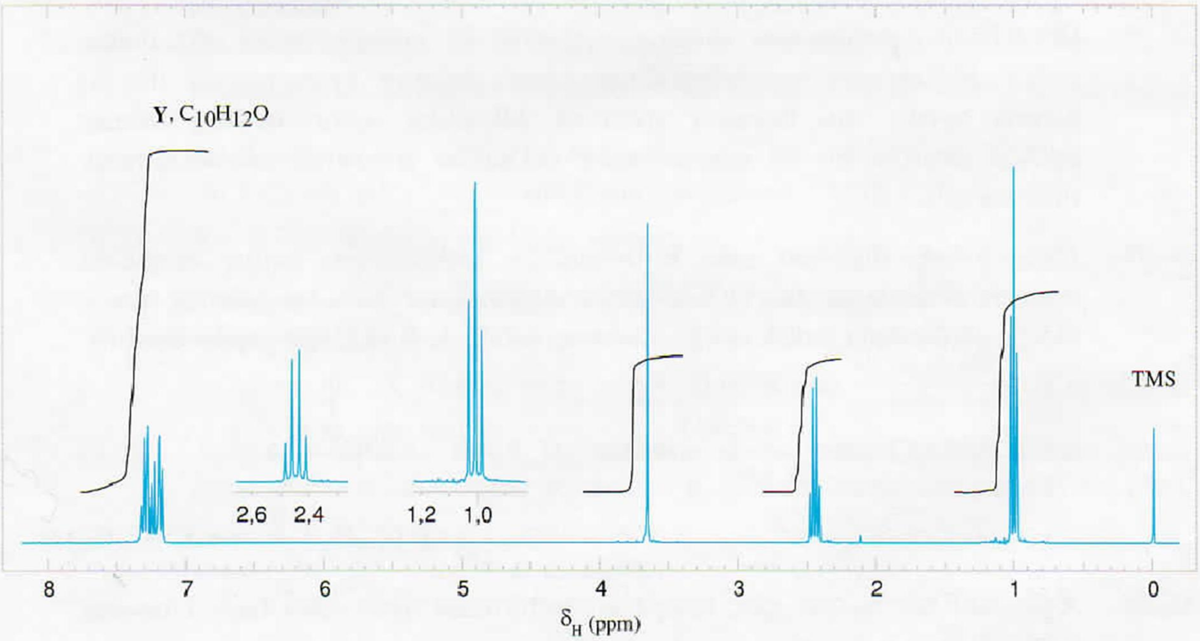


Ftalik asit

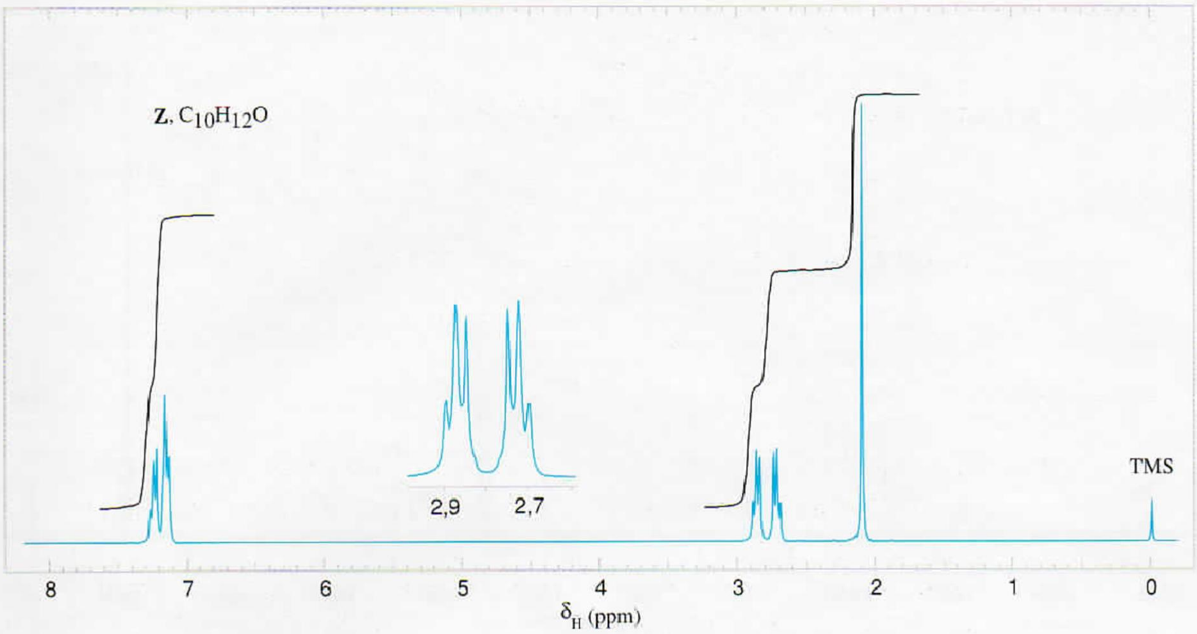
16.41 **Compound W is**



16.42 **Y** ve **Z** bileşikleri $C_{10}H_{12}O$ formülüne sahip izomerlerdir. Her bir bileşiğin İR spektrumu 1710 cm^{-1} civarında kuvvetli bir soğurma bandı verir. **Y** ve **Z**'nin ^1H NMR spektrumu Şekil 16.4 ve Şekil 16.5'te verilmiştir. **Y** ve **Z** için yapılar öneriniz.

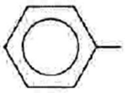
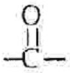


Şekil 16.4 Y Bileşiğinin 300 MHz ^1H NMR spektrumu (Problem 16.42). Sinyallerin genişletilmiş şekilleri kaydırılmış olarak ayrıca gösterilmiştir.



Şekil 16.5 **Z Bileşiğinin 300 MHz ^{1}H NMR spektrumu (Problem 16.42). Sinyallerin genişletilmiş şekilleri kaydırılmış olarak ayrıca gösterilmiştir.**

16.42 Each ^{1}H NMR spectrum (Figs. 16.4 and 16.5) has a five-hydrogen peak near δ 7.2, suggesting the **Y** and **Z** each has a C_6H_5-group. The IR spectrum of each compound shows a strong peak near 1710 cm^{-1}. This absorption indicates that each compound has a C=O group not adjacent to the phenyl group. We have, therefore, the following pieces,

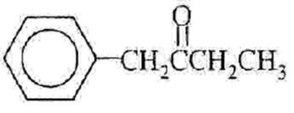

and

$-\overset{O}{\overset{\|}{C}}-$

If we subtract the atoms of these pieces from the molecular formula,

$$\begin{array}{ll} & C_{10}H_{12}O \\ - & \underline{C_7H_5O} \quad (C_6H_5 + C{=}O) \end{array}$$

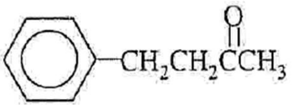
We are left with, C_3H_7

In the ^{1}H NMR spectrum of **Y**, we see an ethyl group [triplet, δ 1.0 (3H) and quartet, δ 2.45 (2H)] and an unsplit $-CH_2-$group [singlet, δ 3.7 (2H)]. This means that **Y** must be



1-Phenyl-2-butanone

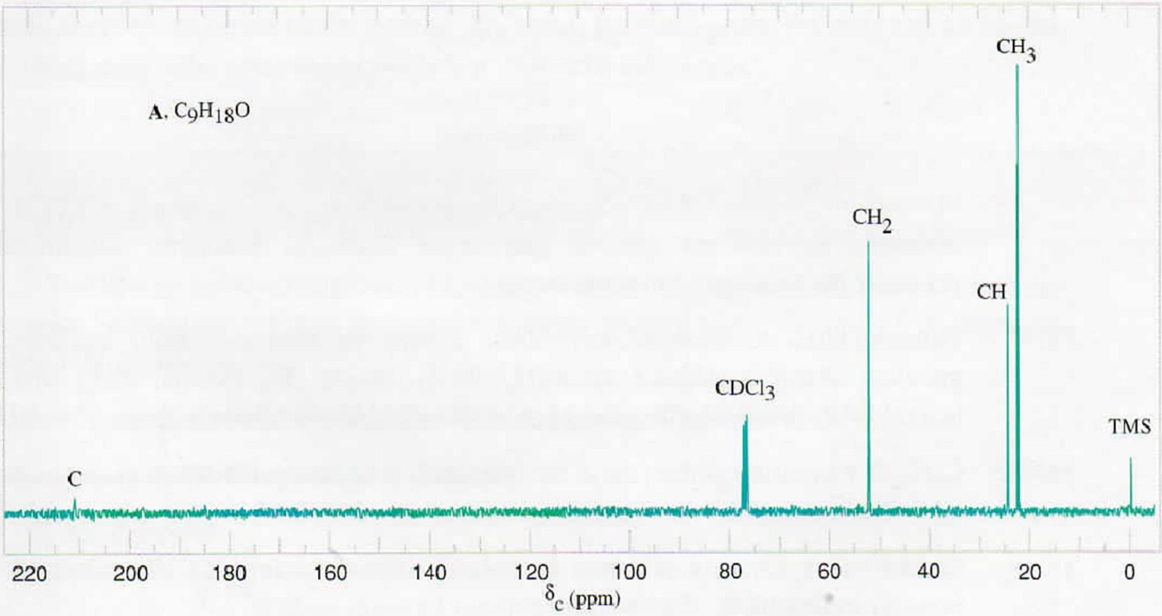
In the ^{1}H NMR spectrum of **Z**, we see an unsplit $-CH_3$ group [singlet, δ 2.1 (3H)] and two triplets at δ 2.7 and 2.9. This means **Z** must be



4-Phenyl-2-butanone

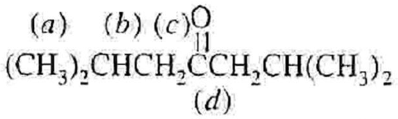
16.43 **A** bileşiği ($C_9H_{18}O$) fenilhidrazon oluşturur fakat olumsuz Tollens testi verir. **A**'nın İR spektrumu 1710 cm^{-1} civarından kuvvetli bir band içerir. **A**'nın

genişband protan-eşleşmesiz ^{13}C NMR, spektrumu Şekil 16.6'da verilmiştir. **A** için bir yapı öneriniz.



Şekil 16.6 A bileşiğinin genişband proton-eşleşmesiz ^{13}C NMR spektrumu (Problem 16.43). DEPT ^{13}C NMR spektrumundan elde edilen bilgiler pikler üzerinde verilmiştir.

16.43 That compound **A** forms a phenylhydrazone, gives a negative Tollens' test, and gives an IR band near 1710 cm^{-1} indicates that **A** is a ketone. The ^{13}C spectrum of **A** contains only four signals indicating that A has a high degree of symmetry. The information from the DEPT ^{13}C NMR spectra enables us to conclude that **A** is diisobutyl ketone:



$$\overset{(a)}{(CH_3)_2}\overset{(b)}{CH}\overset{(c)}{CH_2}\underset{(d)}{\overset{O}{\overset{\|}{C}}}CH_2CH(CH_3)_2$$

Assignments:

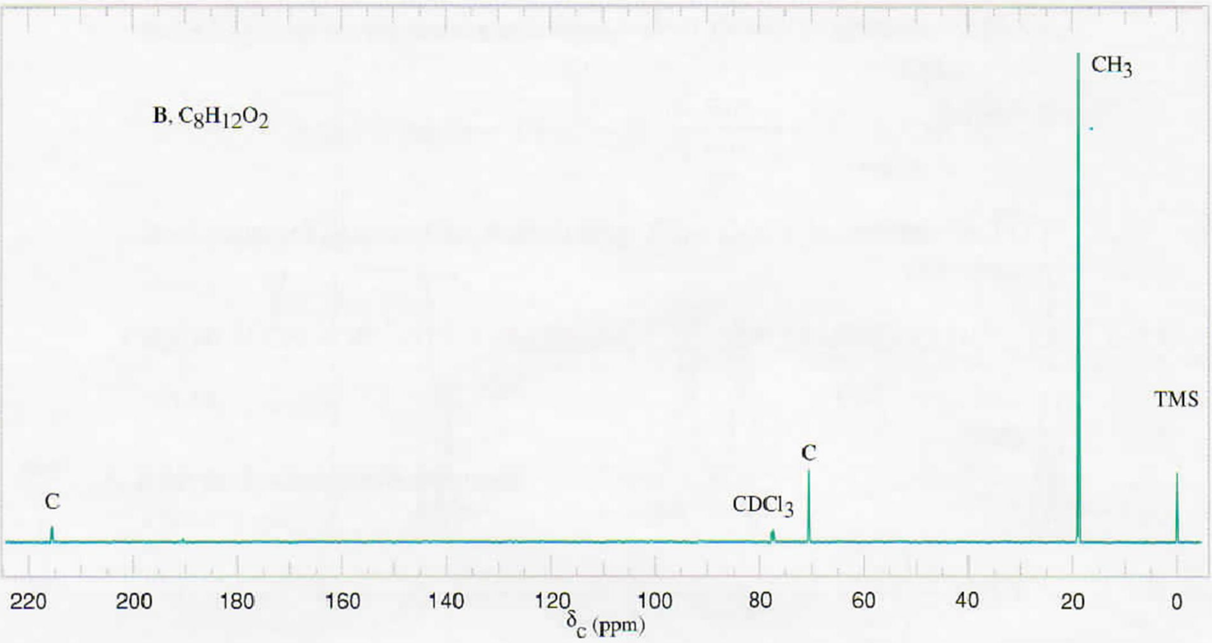
(*a*) δ 22.6

(*b*) δ 24.4

(*c*) δ 52.3

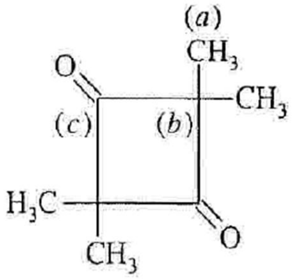
(*d*) δ 210.0

16.44 **B** bileşiği ($C_8H_{12}O_2$) İR spektrumunda kuvvetli bir karbonil soğurması gösterir. **B**'nin genişband proton-eşleşmesiz ^{13}C NMR spektrumu Şekil 16.7'de verilmiştir. **B** için bir yapı öneriniz.



Şekil 16.7 B bileşiğinin geniş band protonu eşleşmesiz ^{13}C NMR spektrumu, Problem 16.44. DEPT ^{13}C NMR spektrumundan elde edilen bilgiler pikler üzerinde verilmiştir.

16.44 That the ^{13}C spectrum of **B** contains only three signals indicates that **B** has a highly symmetrical structure. The information from DEPT spectra indicates the presence of equivalent methyl groups (CH_3 at δ 18.8), equivalent $-\overset{|}{\underset{|}{C}}-$ groups (at δ 70.4), and equivalent $\rangle C{=}O$ groups (at δ 215.0). These features allow only one possible structure for **B**:



Assignments:

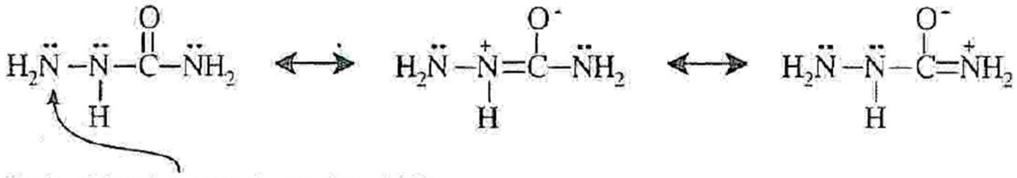
(*a*) δ 18.8

(*b*) δ 70.4

(*c*) δ 215.0

16.45 Semikarbazit ($H_2NNHCONH_2$) bir ketonla (veya bir aldehitle) tepkimeye girdiğinde bir semikarbazon (Altbölüm 16.8A) oluşur. Bu tepkimede semikarbazitin yalnızca bir azot atomu nükleofil olarak davranır ve ketonun karbonil karbonuna atak yapar. Bu tepkimenin ürünü $R_2C{=}NCONHNH_2$'den daha çok $R_2C{=}NNHCONH_2$'dir. Semikarbazitin iki azot atomunun bağıl olarak daha az nükleofilik olduğu bu durumdan sorumlu olan etken nedir?

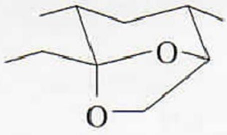
16.45 The two nitrogen atoms of semicarbazide that are adjacent to the C=O group bear partial positive charges because of resonance contributions made by the second and third structures below.



O
$H_2\ddot{N}-\ddot{N}-C-\ddot{N}H_2$
H
O⁻
$H_2\ddot{N}-\overset{+}{N}=C-\ddot{N}H_2$
H
O⁻
$H_2\ddot{N}-\ddot{N}-C=\overset{+}{N}H_2$
H

Only this nitrogen is nucleophilic.

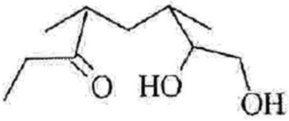
16.46 Hollanda karaağaç hastalığına, karaağaç kabuk böceği tarafından karaağaca aktarılan bir mantar neden olur. Dişi böcek güzel bir karaağaça yerleştiğinde aşağıda yapısı verilen multistriatin de dahil olmak üzere bir çok feromon salgılar. Bu feromonlar, beraberinde öldürücü mantar getiren erkek böcekleri çeker.



Multistriatin

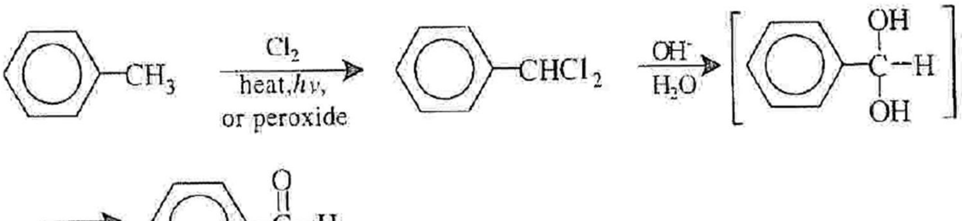
Multistriatinin oda sıcaklığında seyreltik sulu asitlerle etkileştirilmesi, 1715 cm^{-1} civarında kuvvetli bir infrared piki veren $C_{10}H_{20}O_3$ ürününün oluşumuna yol açar. Bu ürün için bir yapı öneriniz.

16.46 Hydrolysis of the acetal linkage of multistriatin produces the ketodiol below.



16.47 Benzaldehitin endüstriyel sentezinde toluen ve klor molekülü başlangıç maddesi olarak kullanılır ve $C_6H_5CHCl_2$ oluşur. Bu bileşik daha sonra benzaldehite dönüştürülür. Bu işlemin içerdiği basamakları yazınız.

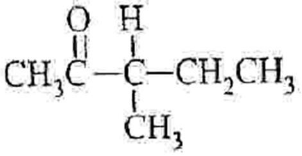
16.47



The *gem*-diol formed in the alkaline hydrolysis step readily loses water to form the aldehyde.

16.48 $C_6H_{12}O$ formüllü optikçe aktif bir bileşik 2,4-dinitrofenilhidrazin ile olumlu, fakat Tollens reaktifi ile olumsuz test sonuçları verir. Bu bileşiğin yapısı nedir?

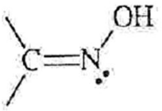
16.48



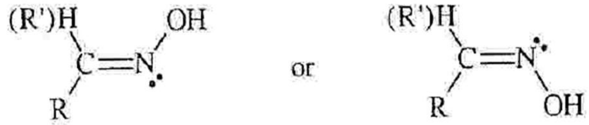
$$CH_3\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{\overset{H}{\overset{|}{C}}}}-CH_2CH_3$$ or its enantiomer

16.49 Aldehitler ve simetrik olmayan ketonların olması durumunda, oksimlerin iki izomeri mümkündür. Bu izomerleşmenin kaynağı nedir?

16.49 The general formula for an oxime is

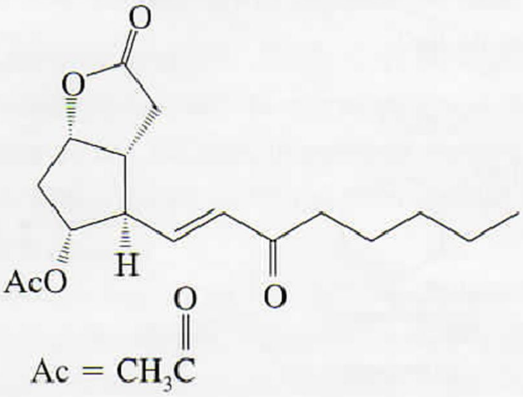


Both carbon and nitrogen are sp^2 hybridized; the electron pair on nitrogen occupies one sp^2 orbital. Aldoximes and ketoximes can exist in either of these two stereoisomeric forms:

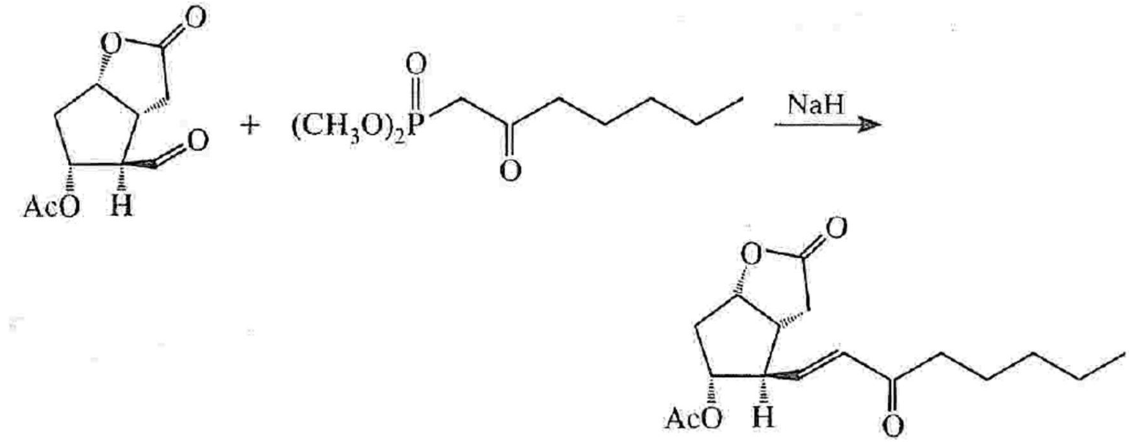


This type of stereoisomerism is also observed in the case of other compounds that possess the C=N group, for example, phenylhydrazones and semicarbazones.

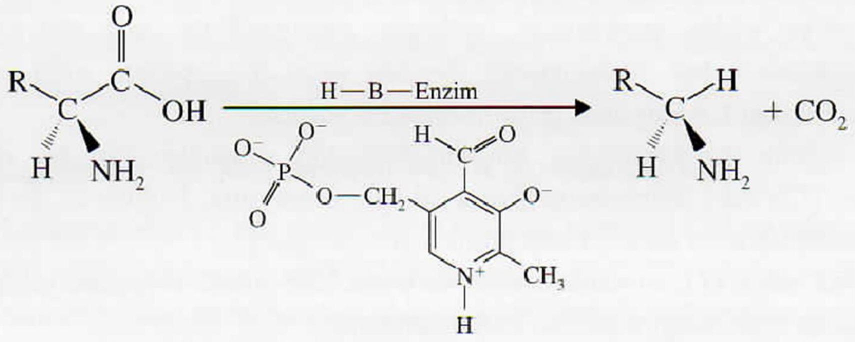
16.50 E. J. Corey (Harvard Üniversitesi) tarafından yapılan prostaglandin $F_{2\alpha}$ ve E_2 sentezinde, aşağıdaki yapı bir ara üründür. Bir Horner – Wadsworth – Emmons tepkimesi (*E*) alkeni oluşturmak için kullanılmıştır. Bu işlemde kullanılan karbonil bileşiğinin ve fosfonat esterinin yapılarını yazınız. (Not: Tepkimenin karbonil bileşeni siklopentil grubu içerir.)



16.50

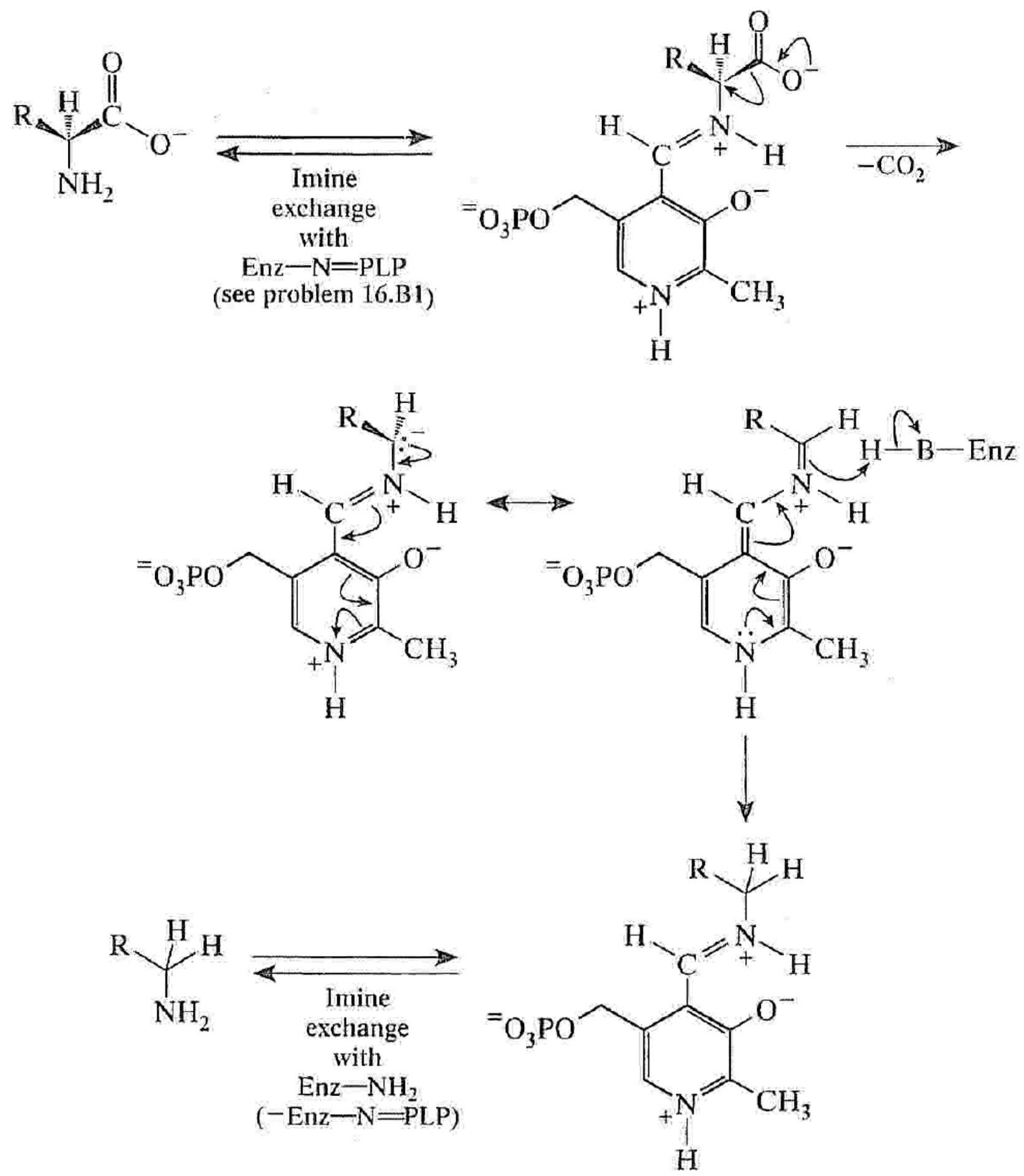


***16.51** Koenzim piridoksal fosfat (PLP, bölüm açılışına ve "Piridoksal Fosfatın Kimyası"na, Altbölüm 16.8, bakınız) bazı α-amino asitlerin dekarboksillenme tepkimelerini katalizler. Diğer tüm PLP tepkimelerindeki gibi işlem PLP ile amino asit arasında bir iminin oluşmasıyla başlar. Mekanizmada, PLP'nin geçici elektron çifti alıcısı olarak kararlı hale getirdiği, amino asidin α-karbonundaki anyon ara ürünü oluşur. Karboksilik asit grubu kaybedilince, yeri, enzim içerisindeki bir bölgedeki (genellikle, bir "H—B—Enzim" grubundan) bir proton tarafından doldurulur. Verilen bu bilgilerle, PLP tarafından katalizlenen α-amino asitlerin dekarboksillenmesi için ayrıntılı bir mekanizma öneriniz.



Piridoksal fosfat

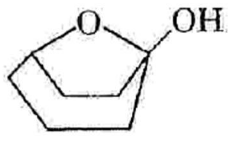
***16.51**


Imine exchange with Enz—N=PLP (see problem 16.B1)
−CO₂
H—B—Enz
Imine exchange with Enz—NH₂ (−Enz—N=PLP)

***16.52** **(a)** 4-Hidroksisikloheptanonun (**A**) infrared spektrumunda beklenilen iki soğurma bandının frekanslarından hangisi daha baskın olabilir. (**b**) Gerçekte, bu ikisinden düşük frekanslı olan band çok zayıftır. **A** ile denge halinde bulunabilen ve bu gözlemleri açıklayan bir izomer yapı çiziniz.

***16.52** (a) O—H stretch at about 3300 cm^{-1}: C=O stretch at about 1710 cm^{-1}

(b)

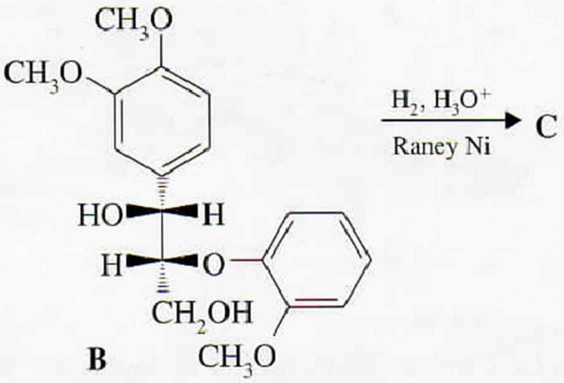


(Intramolecular hemiacetal from *A*)

***16.53** Benzilik alkoller, eterler ve esterlerin önemli tepkimelerinden birisi, hidrojenleme sırasında bezil-oksijen bağının kolay kopmasıdır. Bu, hidrojen tarafından bir bağın koparılmasına yani "hidrojenoliz" e diğer bir örnektir. Bu, asit varlığında kolaylaşır. Hidrojenoliz gergin halkalı bileşiklerde de meydana gelebilir.

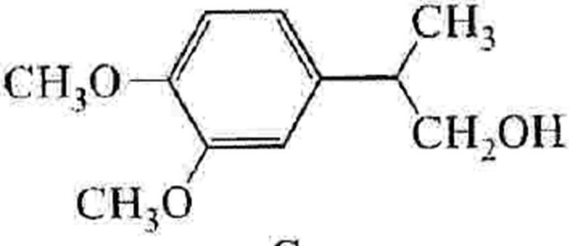
B bileşiğinin (aşağıya bakınız), su ve dioksan içerisindeki hidrojen klorürürün bir seyreltik çözeltisinde Raney nikel katalizörü kullanılarak yapılan hidrojenlendirilmesinde, ürünlerin çoğu yan zincire bağlı 3,4-dimetoksifenil gruplarına sahiptir. Bunların arasında, oluşumunda yalnız hirdojenlenme değil fenil grubunun göçme eğilimini de gösteren ilginç bir ürün, **C**, vardır. **C** ürünü için anahtar spektral değerler aşağıdadır:

MS (*m*/*z*): 196,1084 ($M^{+\cdot}$, yüksek çözünürlükte), 178
İR (cm^{-1}): 3400 (geniş), 3050, 2850 (CH_3-O gerilme)
^{1}**H NMR** (δ, $CHCl_3$'te): 1,21 (i, 3H, J = 7 Hz); 2,25 (b, 1H); 2,83 (ç, 1H); 3,58 (i, 2H, J = 7 Hz); 3,82 (b, 6H); 6,70 (b, 3H).
C bileşiğinin yapısı nedir?



B

***16.53**

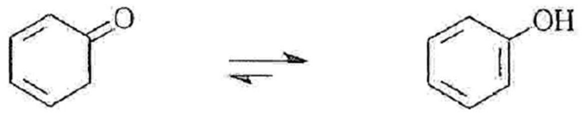


C

Aldehitler ve Ketonlar II. Aldol Tepkimeleri

Problem 17.1 ➤ Tüm pratik amaçlar için, 2,4-sikloheksadien-1-on bileşiği tamamen enol halinde bulunur. 2,4-Sikloheksadien-1-onun yapısını ve enol halini yazınız. Hangi özel etken enol halinin kararlılığını açıklar.

17.1

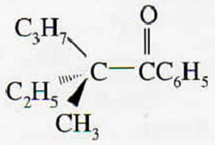


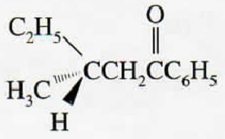
2,4-Cyclohexadien-1-one (keto form)

Phenol (enol form)

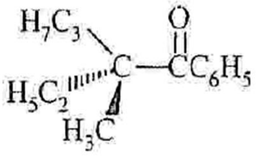
The enol form is aromatic, and it is therefore stabilized by the resonance energy of the benzene ring.

Aşağıdakiler gibi olan optikçe aktif ketonların asit veya baz katalizle rasemleşmeye uğramalarını bekler miydiniz? Cevabınızı açıklayınız. ◄ **Problem 17.2**

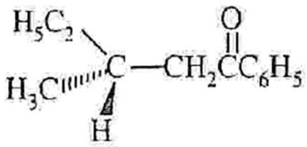




17.2 No.

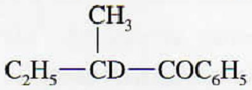


does not have a hydrogen attached to its α-carbon atom (which is a stereocenter) and thus enol formation involving the stereocenter is not possible. With



the stereocenter is a β carbon and thus enol formation does not affect it.

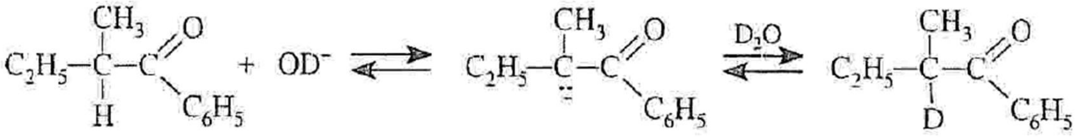
Problem 17.3 ► *sek*-Bütil fenil keton D_2O varlığında OD^- veya D_3O^+ ile etkileştirildiğinde hidrojen-döteryum değişimine uğrar ve aşağıdaki bileşiği oluşturur.



$$C_2H_5-\overset{CH_3}{\overset{|}{C}}D-COC_6H_5$$

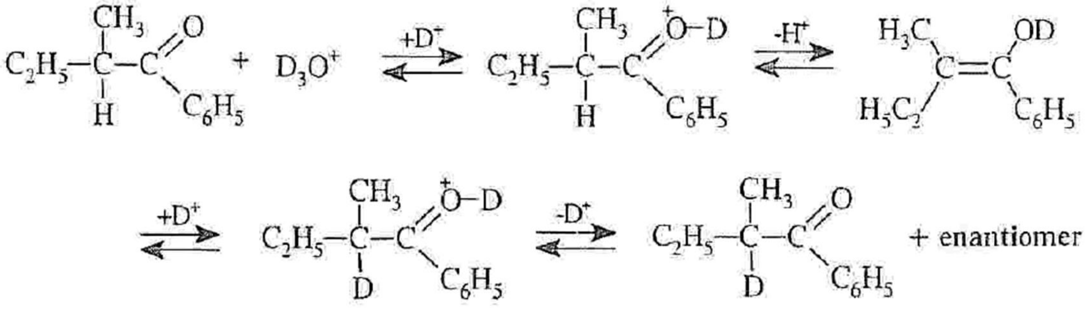
Bu davranışı açıklayan mekanizmalar yazınız.

17.3 In OD^-/D_2O:



+ enantiomer

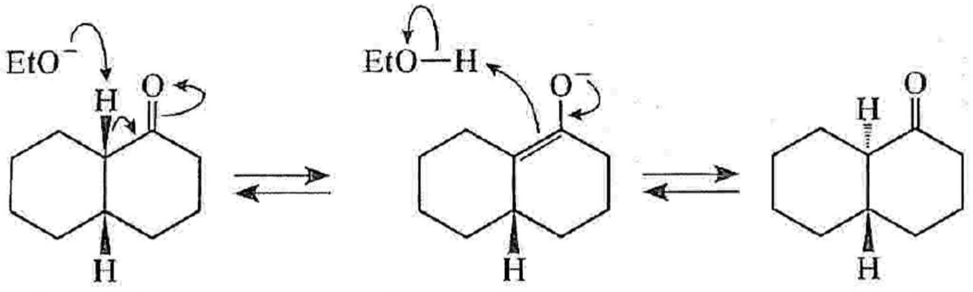
In D_3O^+/D_2O:



+ enantiomer

Problem 17.4 ➤ Etanol içerisindeki sodyum hidroksiti kullanarak *cis*-dekalonun *trans*-dekalona epimerleşmesi için bir mekanizma yazınız. *trans*-Dekalonun *cis*-dekalondan daha kararlı olma nedenini gösteren sandalye konformasyonu yapılarını çiziniz.

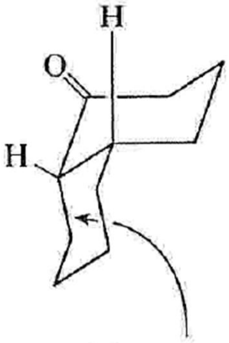
17.4



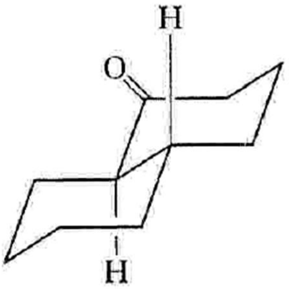
cis-Decalone

Protonation on the bottom face

trans-Decalone



A large group is axial in *cis*-decalone.



No bulky groups are axial in *trans*-decalone.

Ketonların baz içerisindeki halojenlenmesinin neden, "baz katalizli"den daha çok "baz-destekli" olduğunu söyleriz? ◄ **Problem 17.5**

17.5 The reaction is said to be "base promoted" because base is consumed as the reaction takes place. A catalyst is, by definition, not consumed.

Az önce sunduğumuz halojenlenme mekanizmaları için ek kanıtlar şu gerçeklerden elde edilir: (a) Optikçe aktif *sek*-bütil fenil keton, asit-katalizli halojenlenme hızına tam eşdeğer bir hızla asit katalizli rasemleşmeye uğrar. (b) *sek*-Bütil fenil ketonun asit-katalizli iyotlanma tepkimesinin hızı asit-katalizli bromlanmasının hızıyla aynıdır. (c) *sek*-Bütil fenil ketonun baz-katalizli hidrojen-döteryum değişim hızı ile baz-destekli halojenlenme hızı aynıdır. Bu gözlemlerin her birinin sunduğumuz mekanizmaları nasıl desteklediğini açıklayınız. ◄ **Problem 17.6**

17.6 (a) The slow step in base-catalyzed racemization is the same as that in base-promoted halogenation—*the formation of an enolate ion.* (Formation of an enolate ion from *sec*-butyl phenyl ketone leads to racemization because the enolate ion is achiral. When it accepts a proton, it yields a racemic form.) The slow step in acid-catalyzed racemization is also the same as that in acid-catalyzed halogenation—*the formation of an enol.* (The enol, like the enolate ion, is achiral and tautomerizes to yield a racemic form of the ketone.)

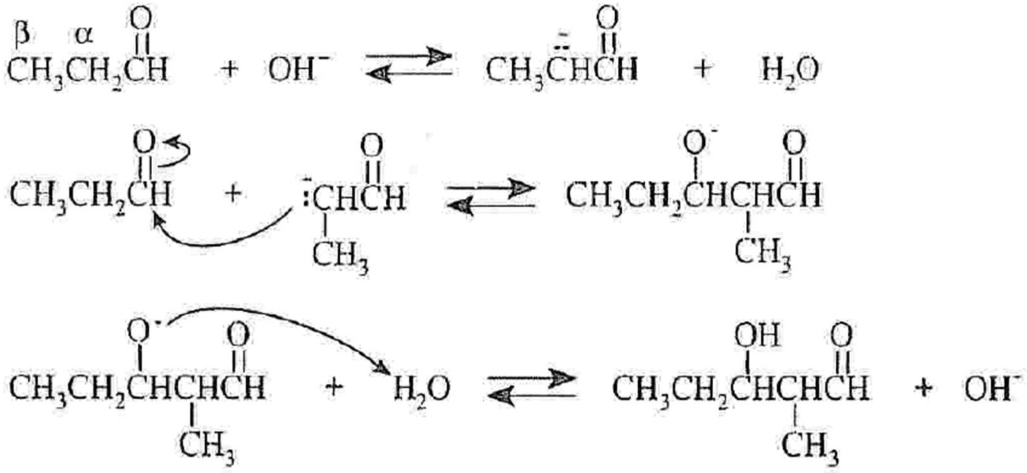
(b) According to the mechanism given, the slow step for acid-catalyzed iodination (formation of the enol) is the same as that for acid-catalyzed bromination. Thus, we would expect both reactions to occur at the same rate.

(c) Again, the slow step for both reactions (formation of the enolate ion) is the same, and consequently, both reactions take place at the same rate.

Problem 17.7 ➤ (a) Propanal $\left(CH_3CH_2\overset{O}{\overset{\|}{C}}H\right)$ bir baz ile etkileştirildiğinde oluşacak aldol katılma tepkimelerindeki tüm basamakları gösteriniz. (b) Aldol katılma ürününün $CH_3CH_2\overset{OH}{\overset{|}{C}}HCH_2CH_2\overset{O}{\overset{\|}{C}}H$ değil de $CH_3CH_2\overset{OH}{\overset{|}{C}}H\underset{CH_3}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}H$ olmasını nasıl açıklarsınız?

(c) Tepkime karışımı ısıtılırsa hangi ürünlerin oluşmasını beklersiniz?

17.7 (a)



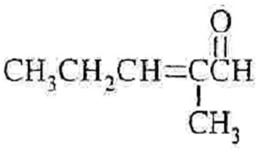
$$\overset{\beta}{CH_3}\overset{\alpha}{CH_2}\overset{O}{\overset{\|}{C}}H + OH^- \rightleftharpoons CH_3\overset{..}{\underset{-}{C}}H\overset{O}{\overset{\|}{C}}H + H_2O$$

$$CH_3CH_2\overset{O}{\overset{\|}{C}}H + \underset{CH_3}{\underset{|}{\bar{:}CH}}\overset{O}{\overset{\|}{C}}H \rightleftharpoons CH_3CH_2\overset{O^-}{\overset{|}{C}}H\underset{CH_3}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}H$$

$$CH_3CH_2\overset{O^-}{\overset{|}{C}}H\underset{CH_3}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}H + H_2O \rightleftharpoons CH_3CH_2\overset{OH}{\overset{|}{C}}H\underset{CH_3}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}H + OH^-$$

(b) For $CH_3CH_2\overset{OH}{\overset{|}{C}}HCH_2CH_2\overset{O}{\overset{\|}{C}}H$ to form, a hydroxide ion would have to remove a β proton in the first step. This does not happen because the anion that would be produced, that is, $\bar{:}CH_2CH_2CHO$, cannot be stabilized by resonance.

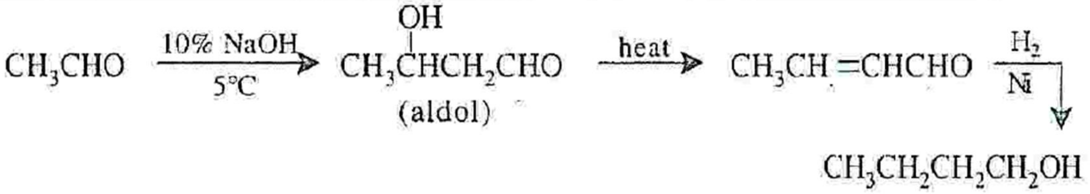
(c)



$$CH_3CH_2CH{=}\underset{CH_3}{\underset{|}{C}}\overset{O}{\overset{\|}{C}}H$$

Problem 17.8 ➤ 1-Bütanolün sentezi için olan endüstriyel süreçlerden birisi asetaldehit ile başlar. Bu sentezin nasıl devam ettirileceğini gösteriniz.

17.8

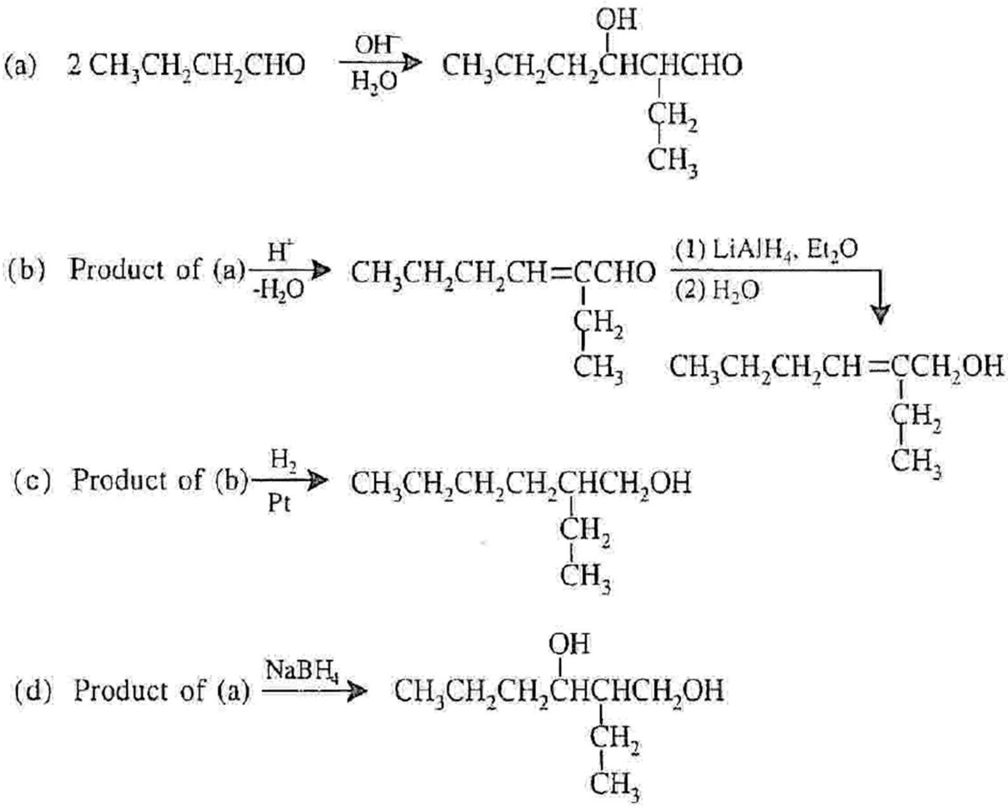


$$CH_3CHO \xrightarrow[5°C]{10\%\ NaOH} \underset{(aldol)}{CH_3\overset{OH}{\overset{|}{C}}HCH_2CHO} \xrightarrow{heat} CH_3CH{=}CHCHO \xrightarrow[Ni]{H_2} CH_3CH_2CH_2CH_2OH$$

Problem 17.9 ➤ Bütanalden başlayarak aşağıdaki her bir ürünün nasıl sentezlenebileceğini gösteriniz.

(a) 2-Etil-3-hidroksiheksanal
(b) 2-Etil-2-heksen-1-ol
(c) 2-Etil-1-heksanol
(d) 2-Etil-1,3-heksandiol (böcek kovucu "6 – 12")

17.9



(a) $2\,CH_3CH_2CH_2CHO \xrightarrow[H_2O]{OH^-} CH_3CH_2CH_2\overset{OH}{C}H\underset{\underset{CH_3}{CH_2}}{C}HCHO$

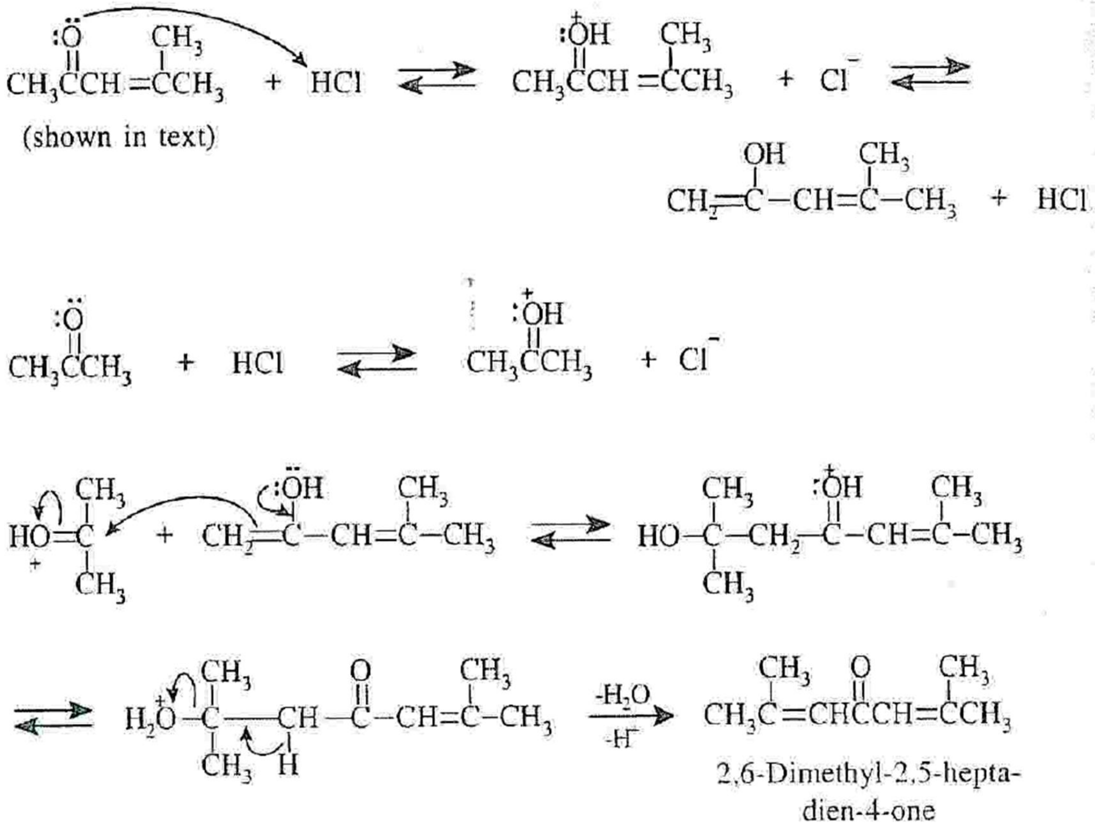
(b) Product of (a) $\xrightarrow[-H_2O]{H^+} CH_3CH_2CH_2CH{=}\underset{\underset{CH_3}{CH_2}}{C}CHO \xrightarrow[(2)\ H_2O]{(1)\ LiAlH_4,\ Et_2O} CH_3CH_2CH_2CH{=}\underset{\underset{CH_3}{CH_2}}{C}CH_2OH$

(c) Product of (b) $\xrightarrow[Pt]{H_2} CH_3CH_2CH_2CH_2\underset{\underset{CH_3}{CH_2}}{C}HCH_2OH$

(d) Product of (a) $\xrightarrow{NaBH_4} CH_3CH_2CH_2\overset{OH}{C}H\underset{\underset{CH_3}{CH_2}}{C}HCH_2OH$

Problem 17.10 ➤ Asetonun asit-katalizli aldol kondensasyonu (az önce gösterildi) bir miktar da 2,6-dimetil-2,5-heptadien-4-on oluşturur. Bu ürünün oluşumu için bir mekanizma yazınız.

17.10



$CH_3\overset{:\ddot{O}}{\overset{\|}{C}}CH{=}\overset{CH_3}{C}CH_3 + HCl \rightleftharpoons CH_3\overset{:\overset{+}{O}H}{\overset{\|}{C}}CH{=}\overset{CH_3}{C}CH_3 + Cl^- \rightleftharpoons CH_2{=}\overset{OH}{C}-CH{=}\overset{CH_3}{C}-CH_3 + HCl$

(shown in text)

$CH_3\overset{:\ddot{O}}{\overset{\|}{C}}CH_3 + HCl \rightleftharpoons CH_3\overset{:\overset{+}{O}H}{\overset{\|}{C}}CH_3 + Cl^-$

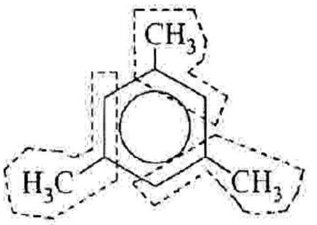
$H\overset{+}{O}{=}\underset{CH_3}{\overset{CH_3}{C}} + CH_2{=}\overset{:\ddot{O}H}{C}-CH{=}\overset{CH_3}{C}-CH_3 \rightleftharpoons HO-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{:\overset{+}{O}H}{\overset{\|}{C}}-CH{=}\overset{CH_3}{C}-CH_3$

$\rightleftharpoons H_2\overset{+}{O}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{H}{CH}-\overset{O}{\overset{\|}{C}}-CH{=}\overset{CH_3}{C}-CH_3 \xrightarrow[-H^+]{-H_2O} CH_3\overset{CH_3}{C}{=}CH\overset{O}{\overset{\|}{C}}CH{=}\overset{CH_3}{C}CH_3$

2,6-Dimethyl-2,5-hepta-dien-4-one

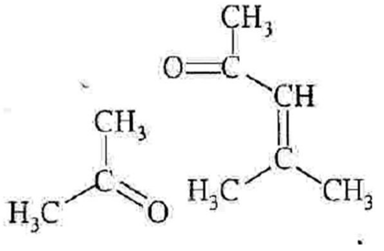
Problem 17.11 ➤ Asetonun sülfürik asitle ısıtılması, mesitilenin (1,3,5-trimetilbenzen) oluşumuna yol açar. Bu tepkime için bir mekanizma öneriniz.

17.11 Drawing the molecules as they will appear in the final product helps to visualize the necessary steps:



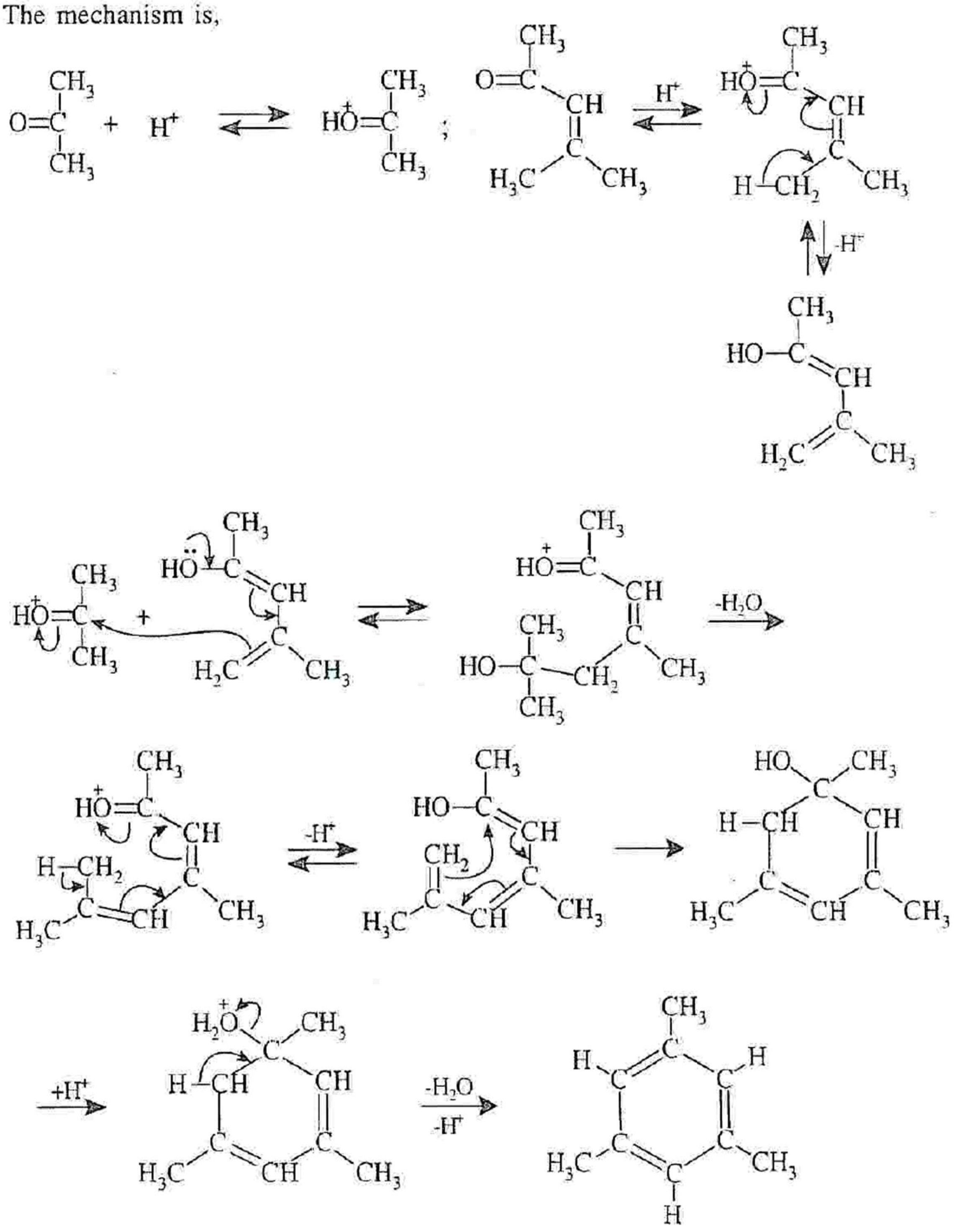
Mesitylene

The two molecules that lead to mesitylene are shown as follows:



This molecule (4-methyl-3-penten-2-one) is formed by an acid-catalyzed condensation between two molecules of acetone as shown in the text.

The mechanism is,



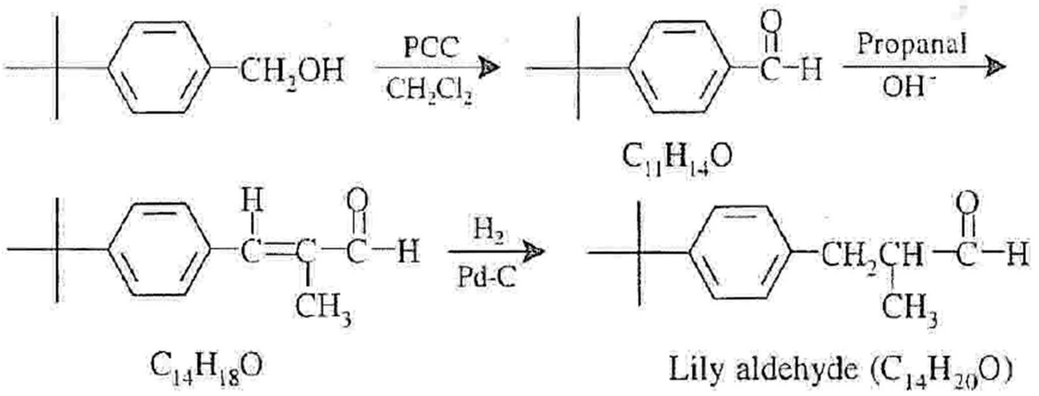
Problem 17.12

Lili aldehit olarak adlandırılan, parfümlerde kullanılan bir bileşiğin sentezinin taslağı aşağıdadır. Eksik yapıların tamamını yazınız.

p-ter-Bütilbenzil alkol $\xrightarrow[CH_2Cl_2]{PCC}$ $C_{11}H_{14}O$ $\xrightarrow[OH^-]{\text{propanal}}$

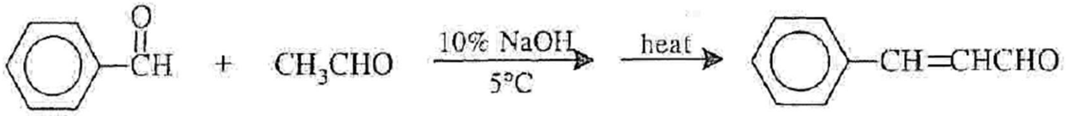
$C_{14}H_{18}O$ $\xrightarrow{H_2,\ Pd-C}$ lili aldehit ($C_{14}H_{20}O$)

17.12

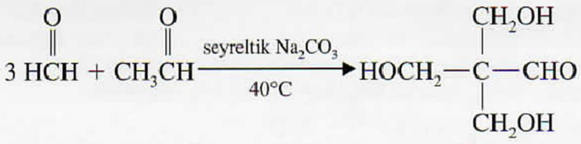


Sinnamaldehit ($C_6H_5CH{=}CHCHO$) sentezi için çapraz aldol tepkimelerinin nasıl kullanılacağını gösteriniz. Tepkime için ayrıntılı bir mekanizma yazınız. ◄ **Problem 17.13**

17.13



Bazik çözeltideki formaldehitin aşırısı asetaldehit ile etkileştirildiğinde aşağıdaki tepkime olur. ◄ **Problem 17.14**

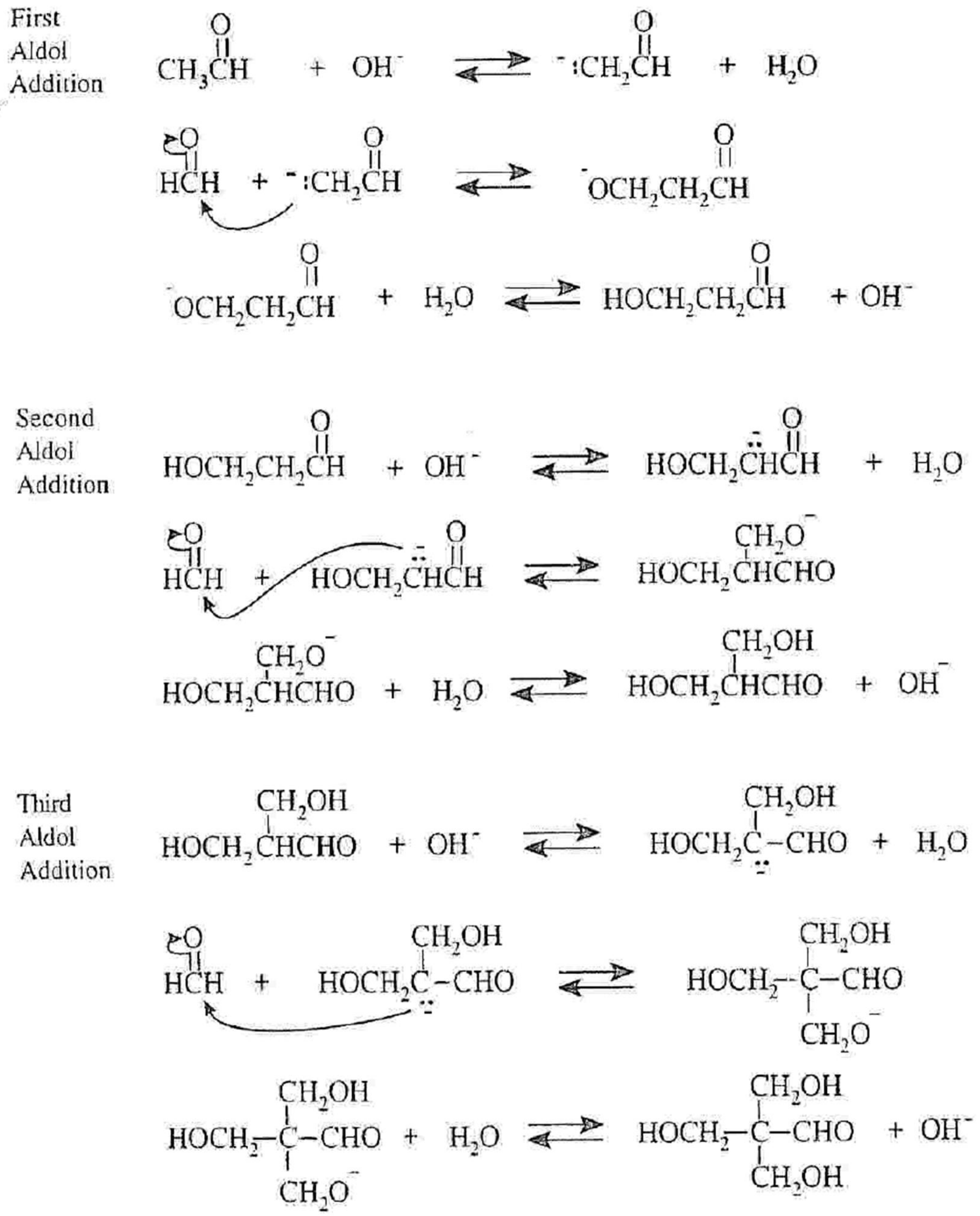


$$3\,H\overset{O}{\overset{\|}{C}}H + CH_3\overset{O}{\overset{\|}{C}}H \xrightarrow[40°C]{\text{seyreltik } Na_2CO_3} HOCH_2-\underset{CH_2OH}{\underset{|}{\overset{CH_2OH}{\overset{|}{C}}}}-CHO$$

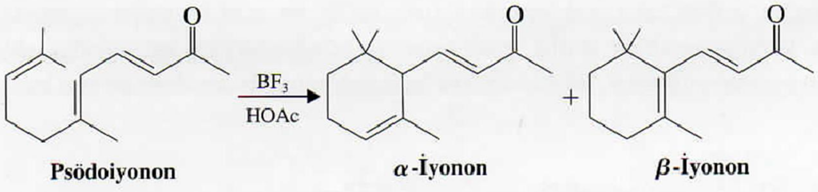
(%82)

Ürün oluşumunu açıklayan bir mekanizma yazınız.

17.14 Three successive aldol additions occur.

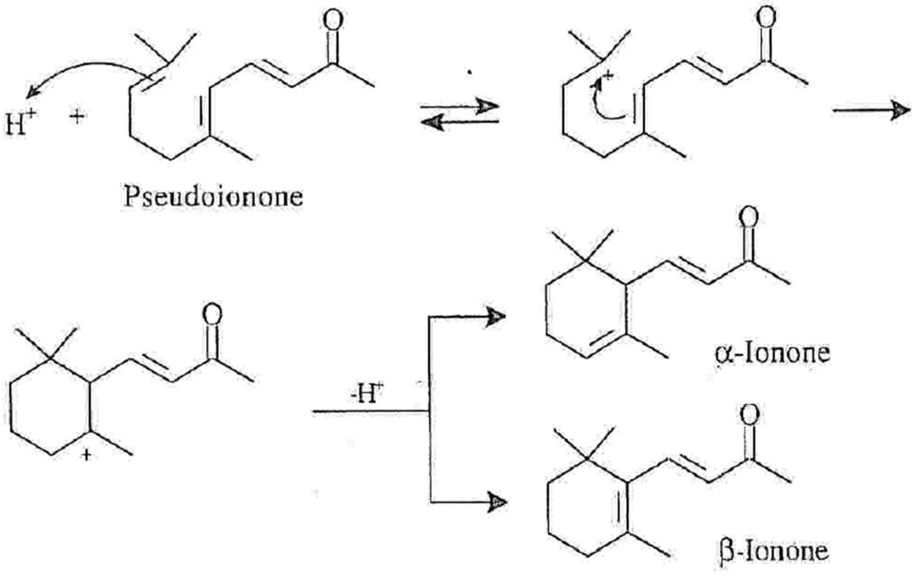


Psödoiyonon, BF_3 ile asetik asit içerisinde etkileştirildiğinde halka kapanması olur ve α ve β-iyononlar oluşur. Bu, A vitamin'nin sentezindeki bir sonraki basamaktır. **◄ Problem 17.15**



(a) α ve β-iyonon oluşumunu açıklayan mekanizmaları yazınız. (b) β-iyonon ana üründür. Bunu nasıl açıklayabilirsiniz? (c) Hangi iyonon UV görünür bölgede daha uzun dalga boyunda soğurma yapar? Niçin?

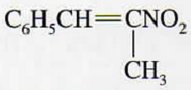
17.15 (a) $CH_3CO_2H + BF_3 \rightleftharpoons CH_3CO_2BF_3^- + H^+$

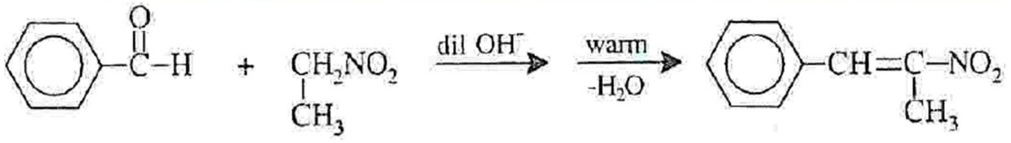


(b) In *β*-ionone both double bonds and the carbonyl group are conjugated; thus it is more stable.

(c) *β*-Ionone, because it is a fully conjugated unsaturated system.

Problem 17.16 ➤ Gerekli aldehit, keton ve nitroalkanın elinizde var olduğunu varsayarak, aşağıdaki her bir bileşiği nasıl sentezleyeceğinizi gösteriniz ve her tepkime için ayrıntılı bir mekanizma yazınız.

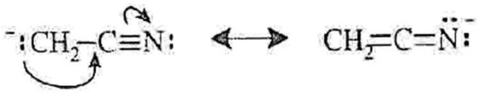
(a) 
$C_6H_5CH{=}\underset{\textstyle CH_3}{\underset{|}{C}}NO_2$ **(b)** $HOCH_2CH_2NO_2$

17.16 (a)


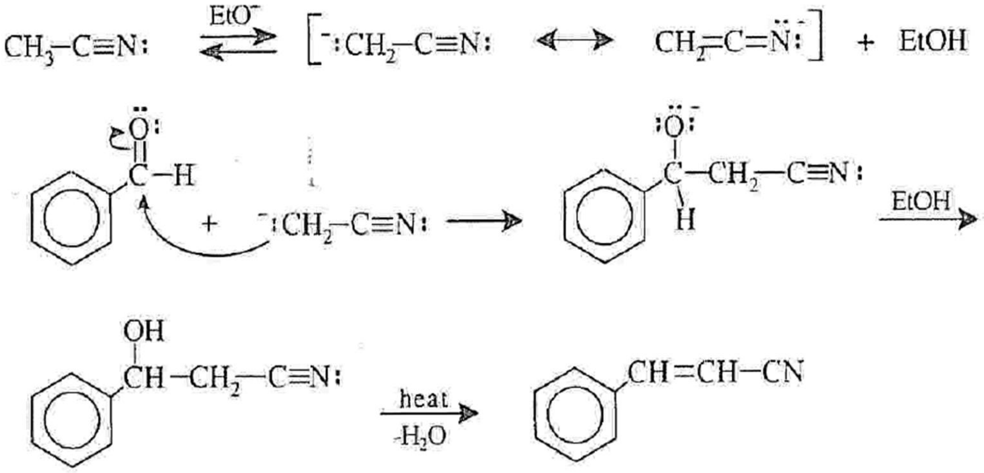
(b)
$H\overset{\overset{\textstyle O}{\|}}{C}H + CH_3NO_2 \xrightarrow{\text{dil OH}^-} HOCH_2CH_2NO_2$

Problem 17.17 ➤ (a) Asetonitrilin etandan çok daha asidik olmasını açıklayan asetonitrilin anyonu için rezonans yapılarını yazınız. (b) Benzaldehit ile asetonitril kondensasyonunun mekanizmasını basamak basamak yazınız.

17.17 (a)

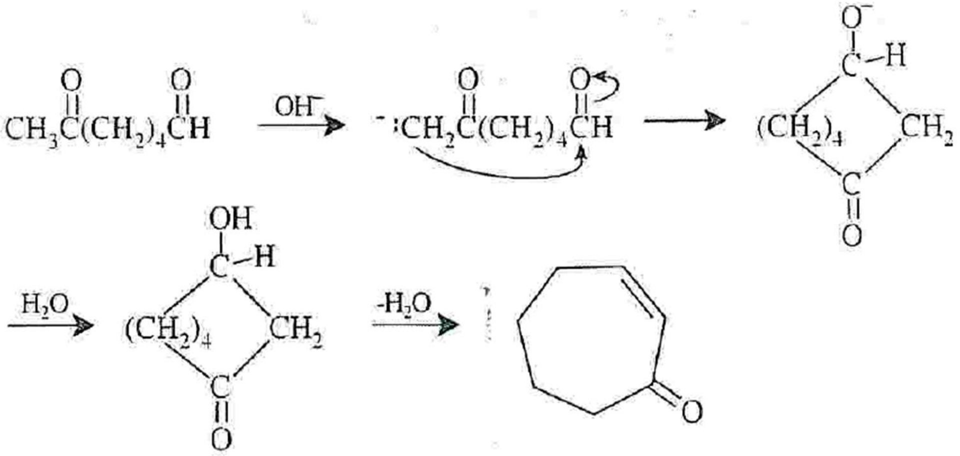


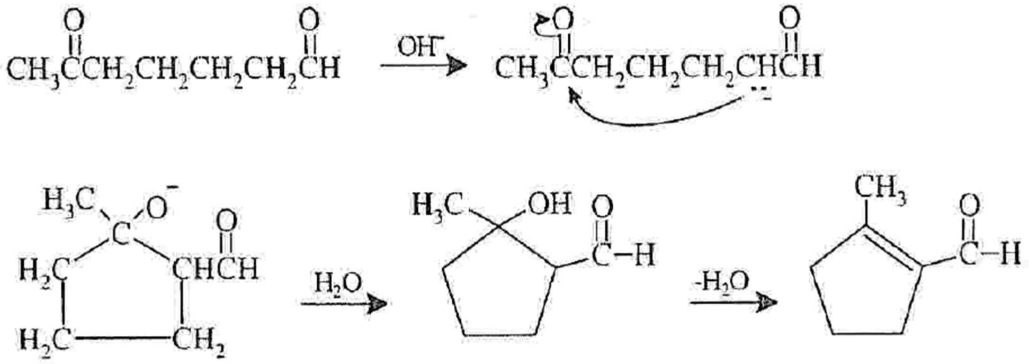
(b)



Her durumda su ayrılmasının meydana geldiğini kabul ederek, bir önceki aldol halkalanmasında oluşabilecek diğer iki ürünün yapısını yazınız. (Bu ürünlerden birisi beş-üyeli halka, diğeri ise yedi üyeli halkaya sahip olacaktır.) **Problem 17.18**

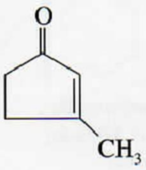
17.18



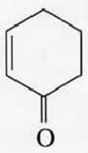


Aşağıdakilerin herbirinin alkol halkalanmasıyla hazırlanmasında hangi başlangıç bileşiğini kullanırdınız? **Problem 17.19**

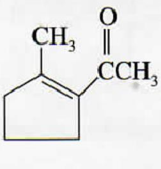
(a)



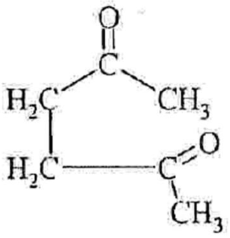
(b)



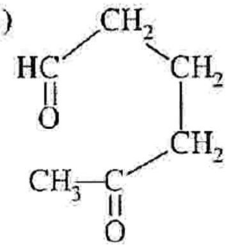
(c)



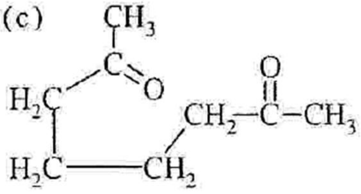
17.19 (a)



(b)



(c)



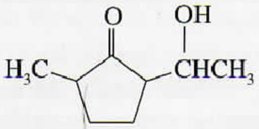
Notice that starting compounds are drawn so as to indicate which atoms are involved in the cyclization reaction.

Problem 17.20 ➤ Hangi deneysel şartlar, moleküller arası kondensasyon sırasında molekül içi aldol tepkimesiyle halkalanma işleminin tercih edilmesini sağlar?

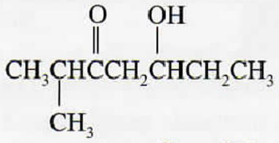
17.20 It is necessary for conditions to favor the intramolecular reaction rather than the intermolecular one. One way to create these conditions is to use very dilute solutions when we carry out the reaction. When the concentration of the compound to be cyclized is very low (i.e., when we use what we call a "high dilution technique"), the probability is greater that one end of a molecule will react with the other end of that same molecule rather than with a different molecule.

Seçeceğiniz ketonlar ve aldehitlerden başlayarak ve lityum enolatlar kullanarak aşağıdakilerin her biri için yönlendirilmiş aldol sentezini gösteriniz. ◀ **Problem 17.21**

(a)

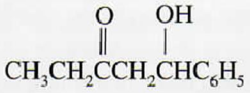


(c)



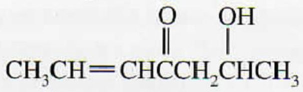
$CH_3\underset{CH_3}{C}H\overset{O}{C}CH_2\overset{OH}{C}HCH_2CH_3$

(b)



$CH_3CH_2\overset{O}{C}CH_2\overset{OH}{C}HC_6H_5$

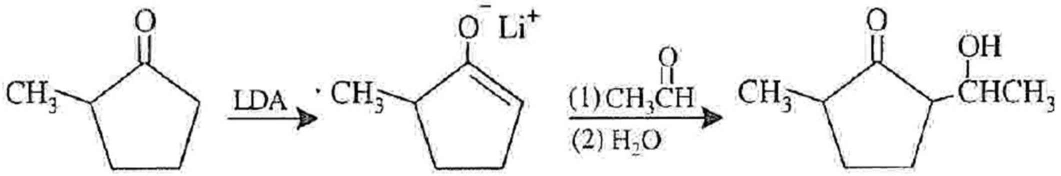
(d)



$CH_3CH{=}CH\overset{O}{C}CH_2\overset{OH}{C}HCH_3$

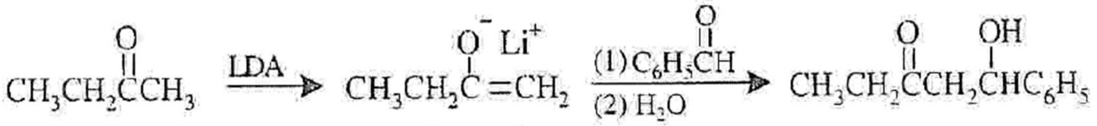
17.21

(a)



Kinetic enolate

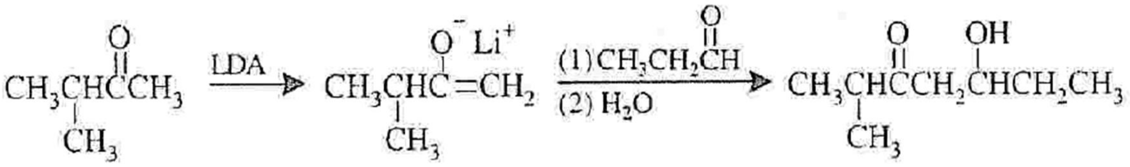
(b)



$CH_3CH_2\overset{O}{C}CH_3 \xrightarrow{LDA} CH_3CH_2\overset{O^-Li^+}{C}{=}CH_2 \xrightarrow[(2)\ H_2O]{(1)\ C_6H_5\overset{O}{C}H} CH_3CH_2\overset{O}{C}CH_2\overset{OH}{C}HC_6H_5$

Kinetic enolate

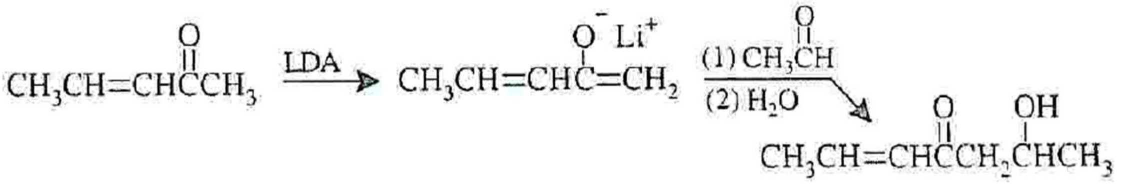
(c)



$CH_3\underset{CH_3}{C}H\overset{O}{C}CH_3 \xrightarrow{LDA} CH_3\underset{CH_3}{C}H\overset{O^-Li^+}{C}{=}CH_2 \xrightarrow[(2)\ H_2O]{(1)\ CH_3CH_2\overset{O}{C}H} CH_3\underset{CH_3}{C}H\overset{O}{C}CH_2\overset{OH}{C}HCH_2CH_3$

Kinetic enolate

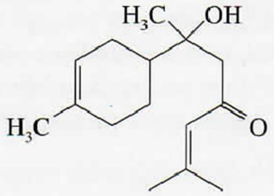
(d)



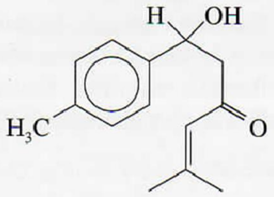
$CH_3CH{=}CH\overset{O}{C}CH_3 \xrightarrow{LDA} CH_3CH{=}CH\overset{O^-Li^+}{C}{=}CH_2 \xrightarrow[(2)\ H_2O]{(1)\ CH_3\overset{O}{C}H} CH_3CH{=}CH\overset{O}{C}CH_2\overset{OH}{C}HCH_3$

Problem 17.22

α-Bisabolanon ve osimenon adlarındaki bileşiklerin her ikisi de yönlendirilmiş aldol sentezi ile sentezlenmişlerdir. Her iki sentezde de kullanılan başlangıç bileşiği $(CH_3)_2C{=}CHCOCH_3$'tür. Siz diğer uygun başlangıç bileşiklerini seçiniz ve (a) α-bisabolanon ve (b) osimenonun sentezini tasarlayınız.

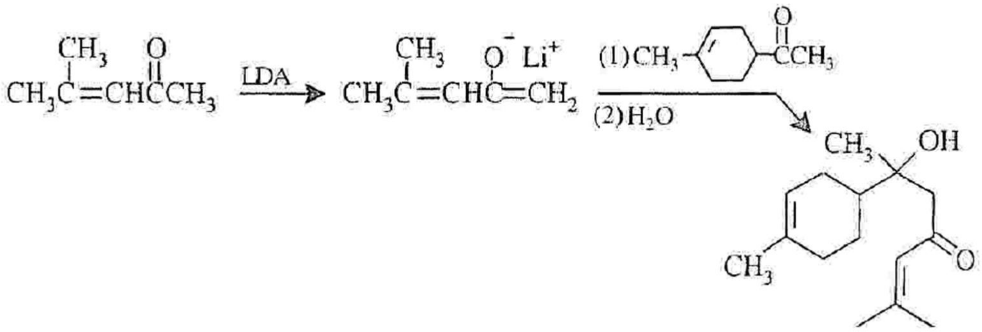


α-Bisabolanon



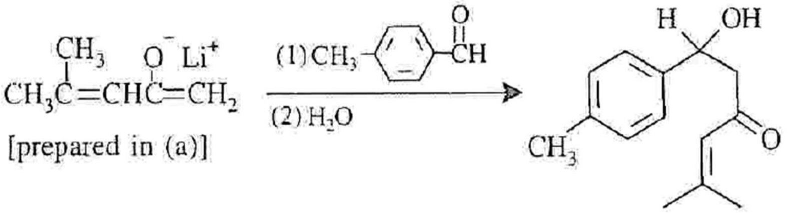
Osimenon

17.22 (a)



α-Bisabolanone

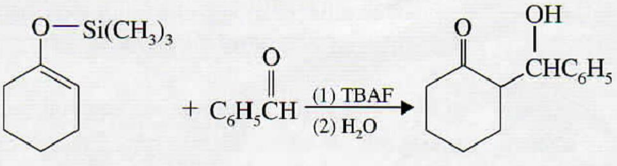
(b)



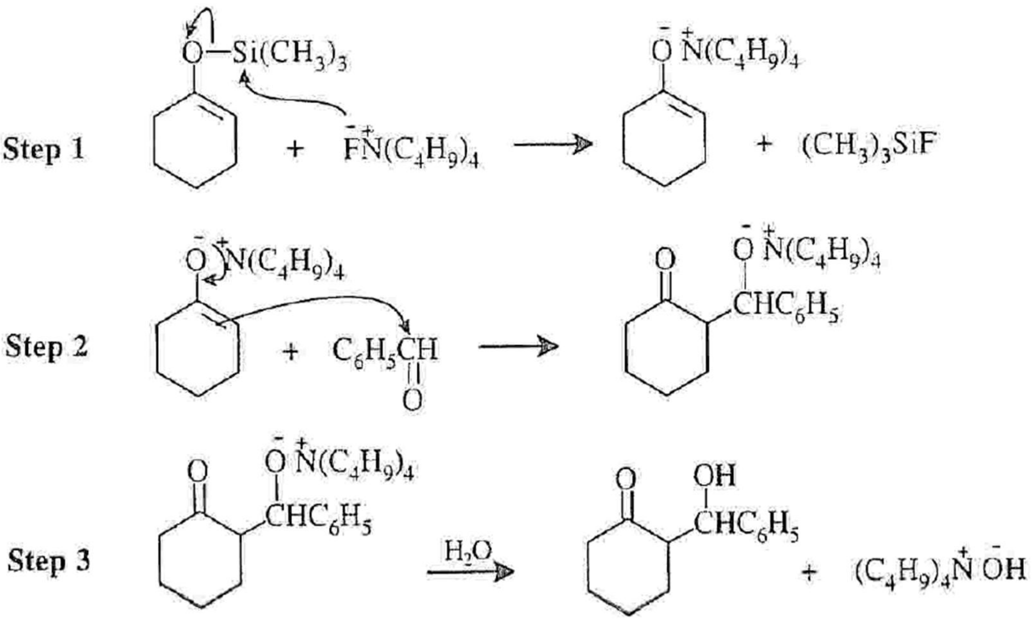
Ocimenone

Problem 17.B1

Sikloheksanondan türetilen trimetilsilil enol eterin benzaldehit ve tetrabütilamonyum florür, $(C_4H_9)_4N^+F^-$ (TBAF olarak kısaltılır) ile etkileştirilmesi aşağıdaki ürünü vermektedir. Bu tepkimede meydana gelen basamakları gösteriniz.

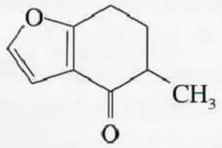


17.B1

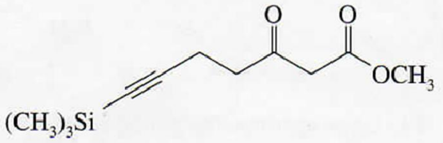


Problem 17.23

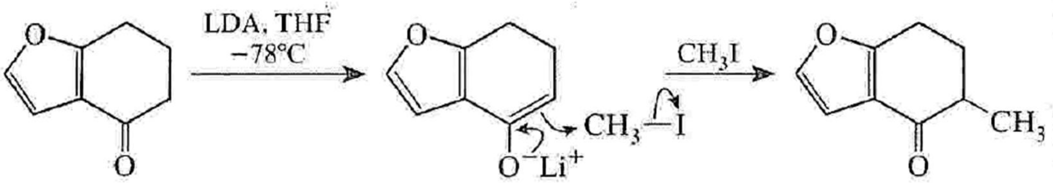
(a) Aşağıdaki bileşiğe (iltihap girderici bir bileşik olan ve kahve çekirdeğinde bulunan kafestolün E. J. Corey tarafından yapılan sentezinde bir ara ürün) bir metil grubu sokmak için lityum enolatın yer aldığı bir tepkime yazınız.



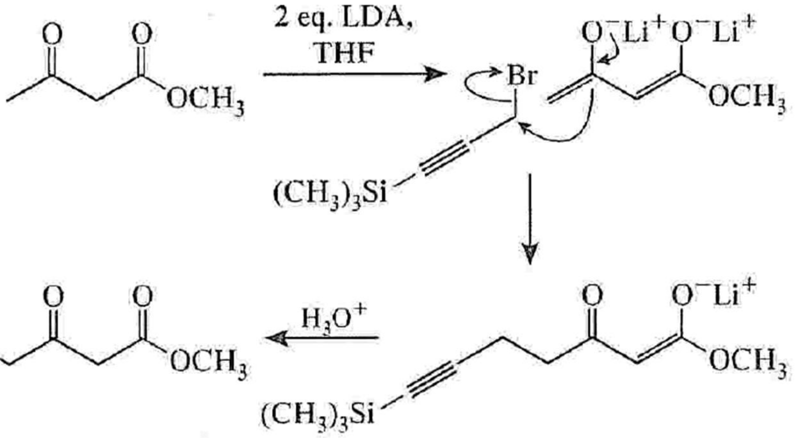
(b) Dienolatlar, LDA'nın iki eşdeğer miktarı kullanılarak β-keto esterlerden oluşturulabilirler. Bu dienolat, iki enolat karbonundan daha bazik olanı üzerinden seçimli olarak alkillendirilebilir. Aşağıdaki bileşiğin bir dienolat ve uygun bir alkil halojenür kullanılarak yapılan sentezi için bir tepkime yazınız.



17.23 (a)

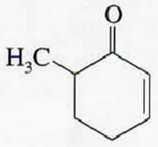


(b)

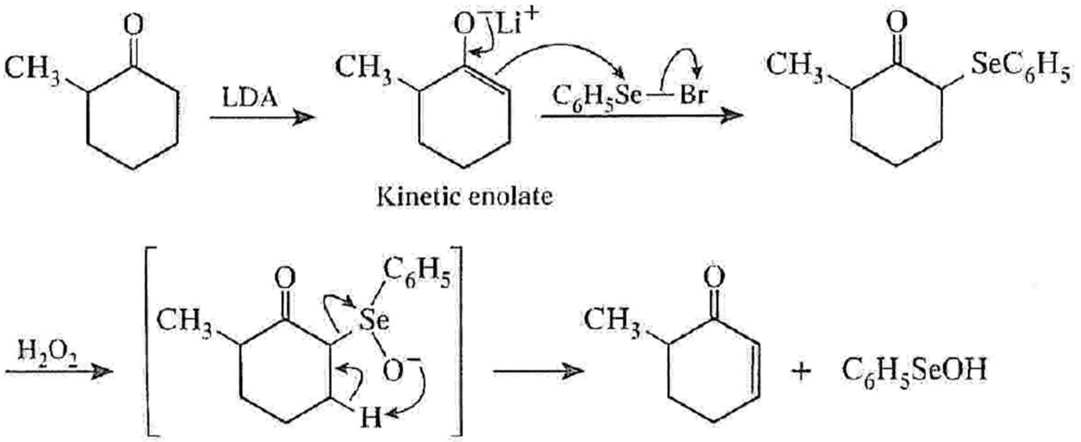


Problem 17.24

2-Metilsikloheksanon ile başlayarak aşağıdaki bileşiğin sentezinde α-selenlemeyi nasıl kullanabileceğinizi gösteriniz.

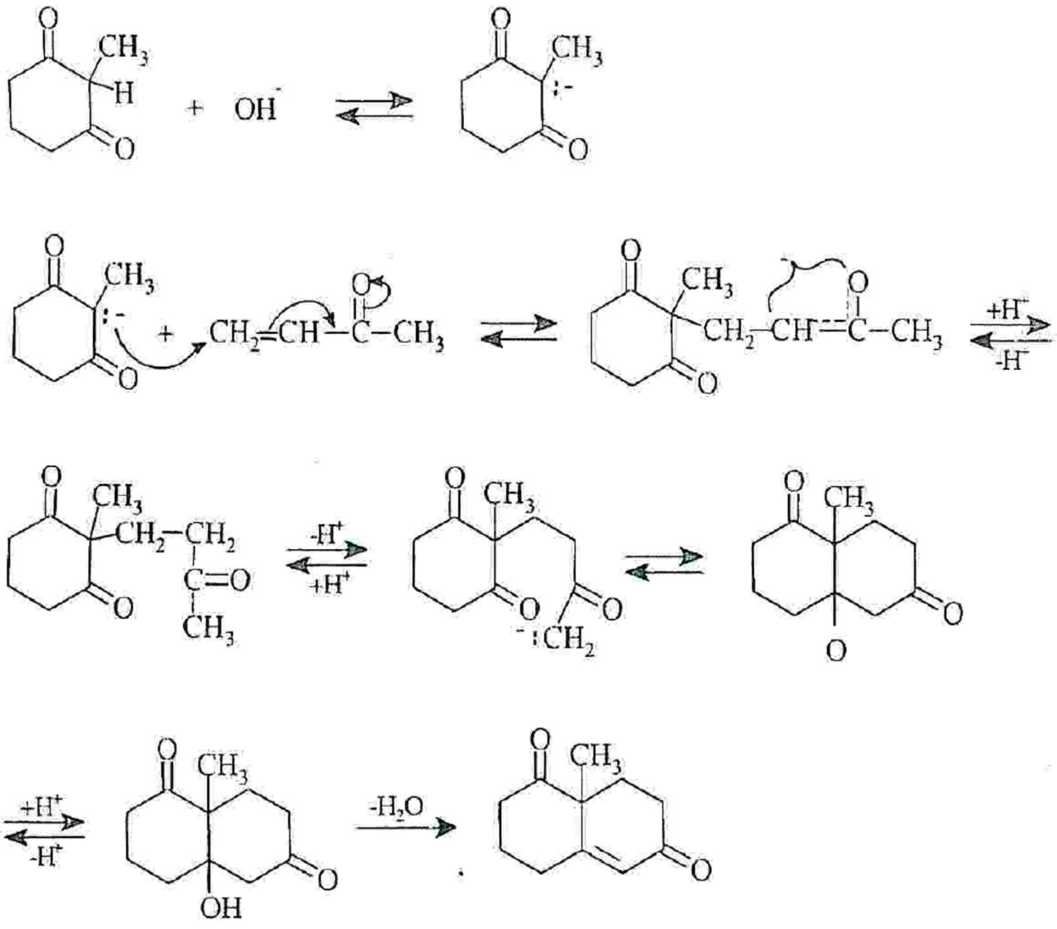


17.24

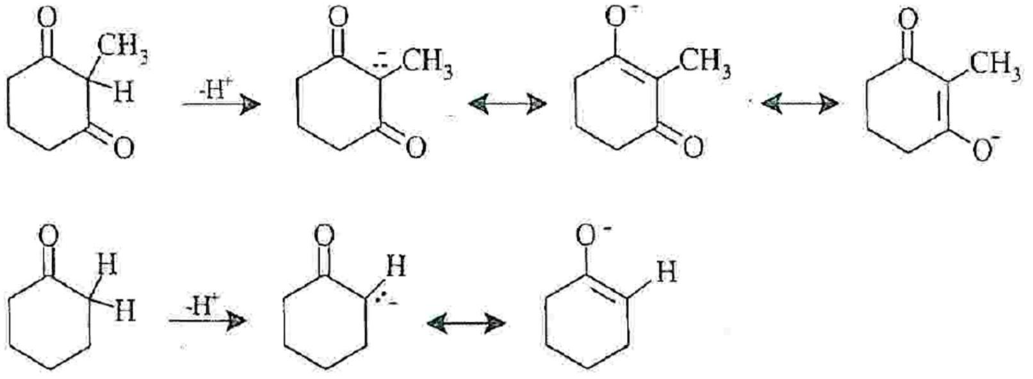


Problem 17.25 ➤ (a) Yukarıda verilen Robinson halkalama tepkimesinin her iki dönüşüm basamağı için uygun mekanizmalar yazınız. (b) 2-Metil-1,3-sikloheksandionun sikloheksanondan daha kuvvetli mi yoksa daha zayıf asit mi olmasını beklersiniz? Cevabınızı açıklayınız.

17.25 (a)

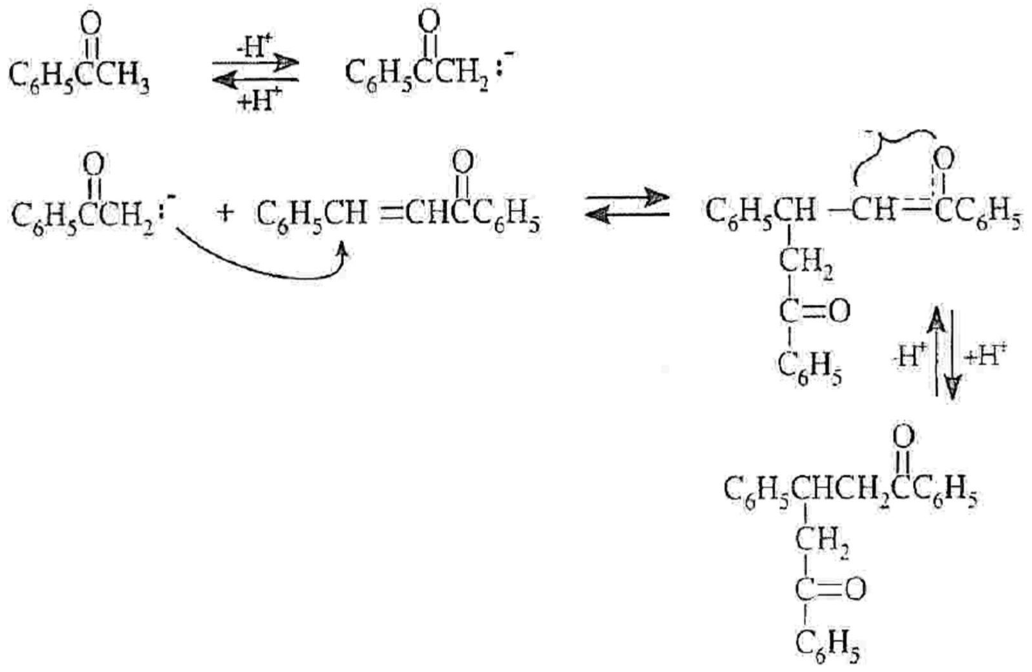


(b) 2-Methyl-1,3-cyclohexanedione is more acidic because its enolate ion is stabilized by an additional resonance structure.

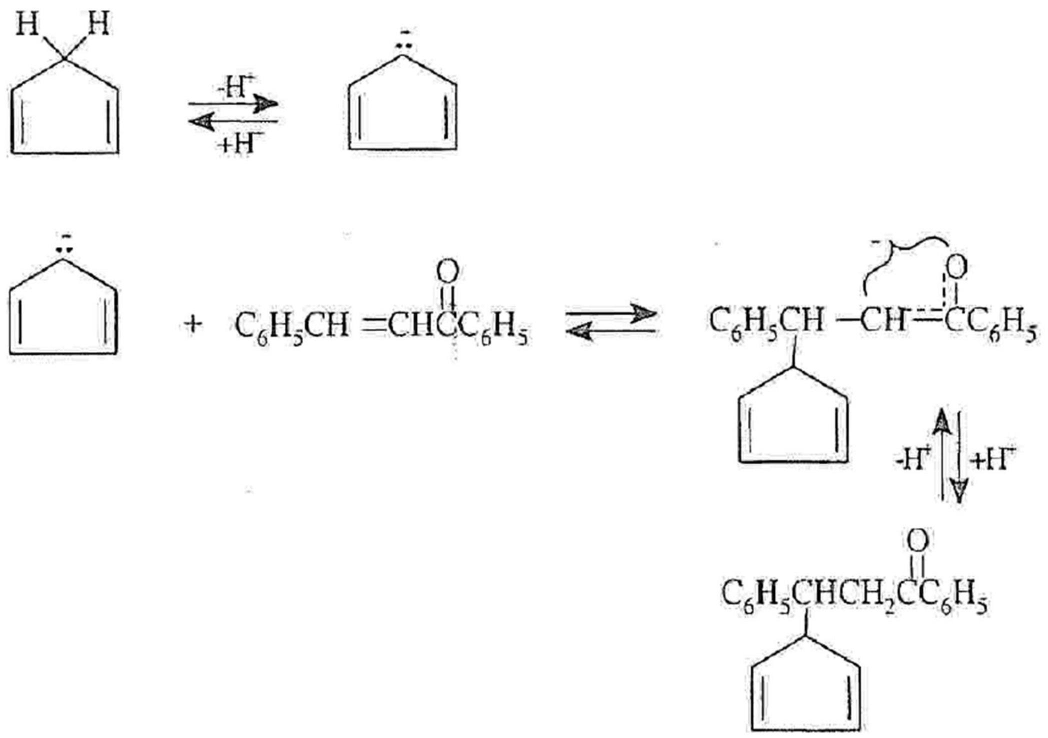


Problem 17.26 ➤ (a) 1,3-Difenil-2-propen-1-on (Altbölüm 17.5B) ve asetofenonun (b)1,3-difenil-2-propen-1-on ve siklopentadienin baz katalizli Michael katılmasından hangi ürünü elde edeceğinizi umarsınız? Her bir mekanizmada tüm basamakları gösteriniz.

17.26 (a)

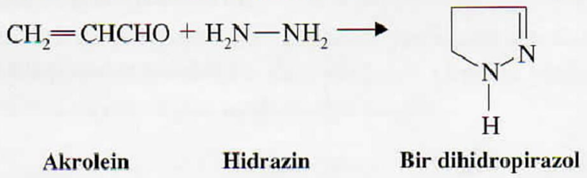


(b)



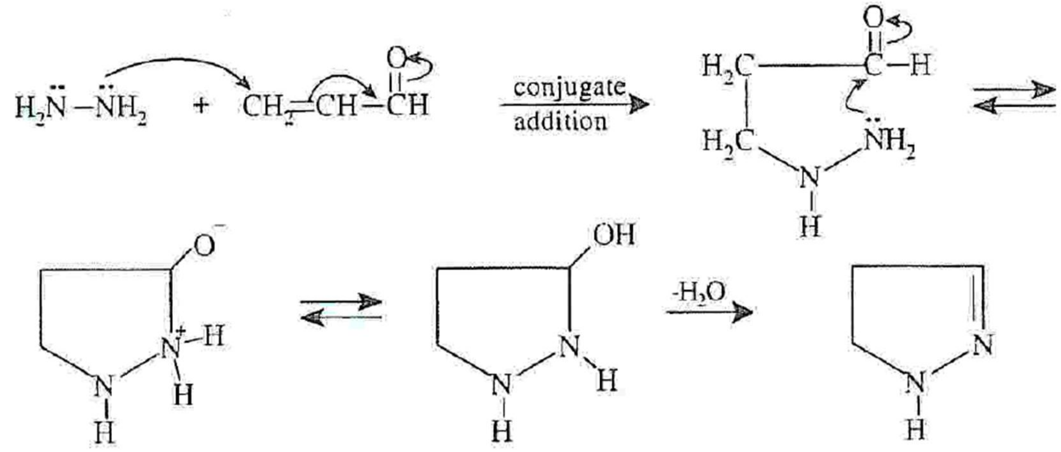
Problem 17.27

Akrolein, hidrazin ile tepkimeye girdiğinde ürün bir dihidropirazoldur:



Bu tepkimeyi açıklayan bir mekanizma öneriniz.

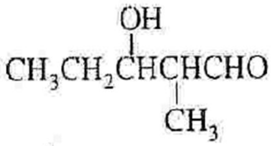
17.27



17.28 Propanal aşağıda verilen her bir reaktifle etkileştirildiğinde oluşan tepkime (eğer olursa) ürünlerinin yapı formüllerini yazınız.

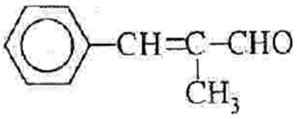
- **(a)** OH^-, H_2O
- **(b)** C_6H_5CHO, OH^-
- **(c)** HCN
- **(d)** $NaBH_4$
- **(e)** $HOCH_2CH_2OH$, p-TsOH
- **(f)** Ag_2O, OH^-, sonra H_3O^+
- **(g)** CH_3MgI, sonra H_3O^+
- **(h)** $Ag(NH_3)_2{}^+OH^-$, sonra H_3O^+
- **(i)** NH_2OH
- **(j)** $C_6H_5\overset{-}{C}H-\overset{+}{P}(C_6H_5)_3$
- **(k)** C_6H_5Li, sonra H_3O^+
- **(l)** $HC\equiv CNa$, sonra H_3O^+
- **(m)** $HSCH_2CH_2SH$, HA, sonra Raney Ni, H_2
- **(n)** $CH_3CH_2CHBrCO_2Et$ ve Zn, sonra H_3O^+

17.28 (a)

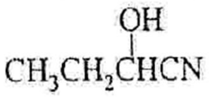


$CH_3CH_2\overset{OH}{C}H\underset{CH_3}{C}HCHO$

(b)



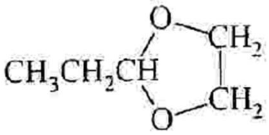
(c)



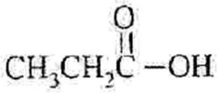
$CH_3CH_2\overset{OH}{C}HCN$

(d) $CH_3CH_2CH_2OH$

(e)

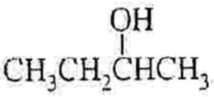


(f)



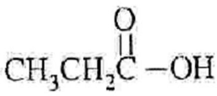
$CH_3CH_2\overset{O}{\overset{\|}{C}}-OH$

(g)



$CH_3CH_2\overset{OH}{C}HCH_3$

(h)

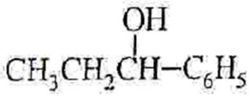


$CH_3CH_2\overset{O}{\overset{\|}{C}}-OH$

(i) $CH_3CH_2CH{=}NOH$

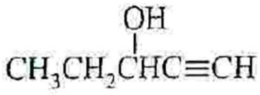
(j) $CH_3CH_2CH{=}CHC_6H_5$

(k)



$CH_3CH_2\overset{OH}{C}H-C_6H_5$

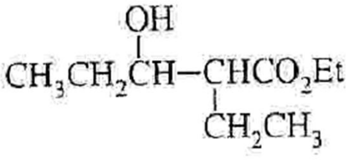
(l)



$CH_3CH_2\overset{OH}{C}HC\equiv CH$

(m) $CH_3CH_2CH_3$

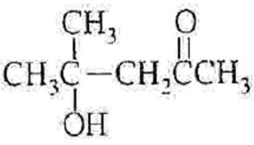
(n)

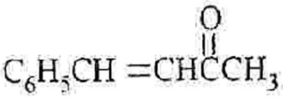


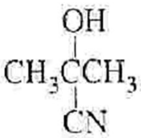
$CH_3CH_2\overset{OH}{C}H-\underset{CH_2CH_3}{C}HCO_2Et$

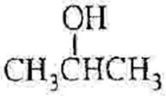
17.29 Asetonun bir önceki reaktiflerin her biriyle etkileştirilmesiyle oluşan tepkime ürünlerinin (eğer olursa) yapı formülleri yazınız.

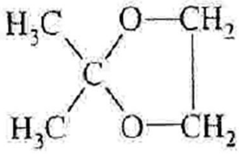
17.29

(a)

$CH_3\overset{CH_3}{\underset{OH}{C}}-CH_2\overset{O}{\overset{\|}{C}}CH_3$

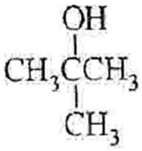
(b)

$C_6H_5CH=CH\overset{O}{\overset{\|}{C}}CH_3$

(c)

$CH_3\overset{OH}{\underset{CN}{C}}CH_3$

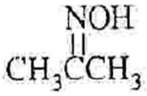
(d)

$CH_3\overset{OH}{C}HCH_3$

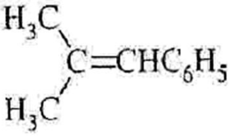
(e)


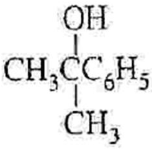
(f) No reaction

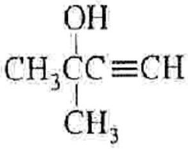
(g)

$CH_3\overset{OH}{\underset{CH_3}{C}}CH_3$

(h) No reaction

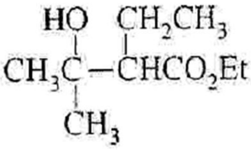
(i)

$CH_3\overset{NOH}{\overset{\|}{C}}CH_3$

(j)


(k)

$CH_3\overset{OH}{\underset{CH_3}{C}}C_6H_5$

(l)

$CH_3\overset{OH}{\underset{CH_3}{C}}C\equiv CH$

(m) $CH_3CH_2CH_3$

(n)

$CH_3\overset{HO}{\underset{CH_3}{C}}-\overset{CH_2CH_3}{C}HCO_2Et$

17.30 4-Metilbenzaldehit aşağıdakilerin her biri ile tepkimeye girdiği zaman hangi ürünler oluşur?

(a) CH_3CHO, OH^-

(b) $CH_3C\equiv CNa$ sonra H_3O^+

(c) CH_3CH_2MgBr, sonra H_3O^+

(d) Soğuk seyreltik $KMnO_4$, OH^-, sonra H_3O^+

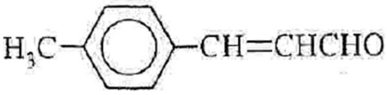
(e) Sıcak $KMnO_4$, OH^- sonra H_3O^+

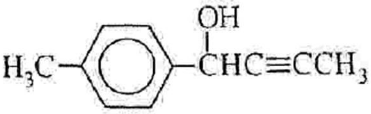
(f) $^-{:}CH_2-\overset{+}{P}(C_6H_5)_3$

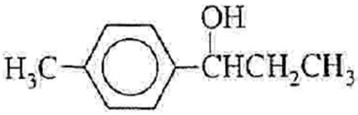
(g) $CH_3COC_6H_5$, OH^-

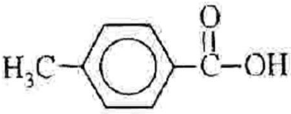
(h) $BrCH_2CO_2Et$ ve Zn sonra H_3O^+

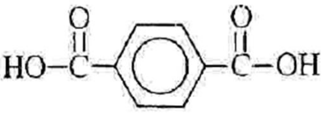
17.30

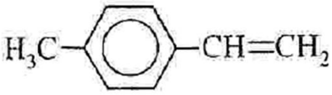
(a)


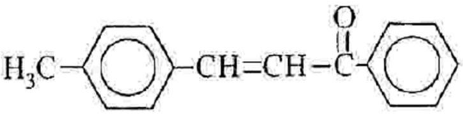
(b)


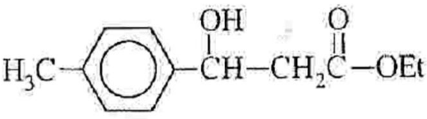
(c)


(d)


(e)


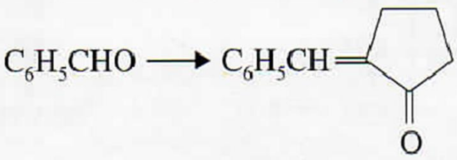
(f)


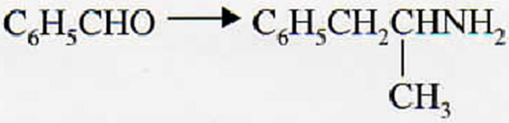
(g)


(h)


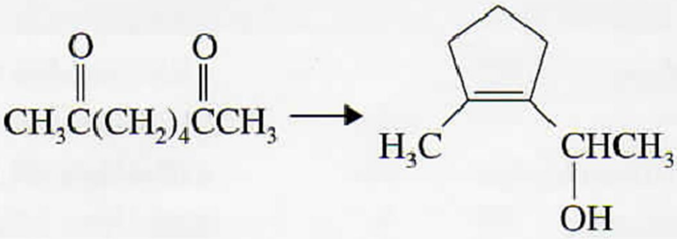
17.31 Aşağıdaki her bir dönüşümün nasıl sağlandığını gösteriniz, gerekli olabilecek diğer reaktifleri kullanabilirsiniz.

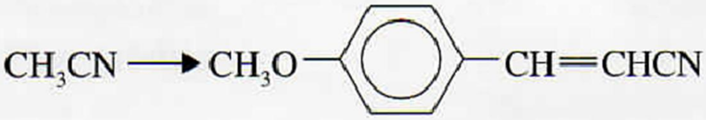
(a) $CH_3COC(CH_3)_3 \longrightarrow C_6H_5CH{=}CHCOC(CH_3)_3$

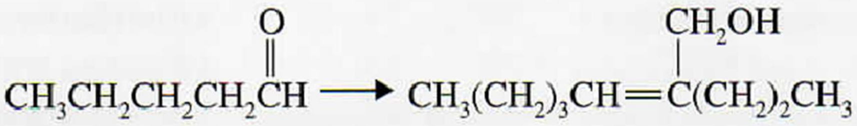
(b) 

(c) 

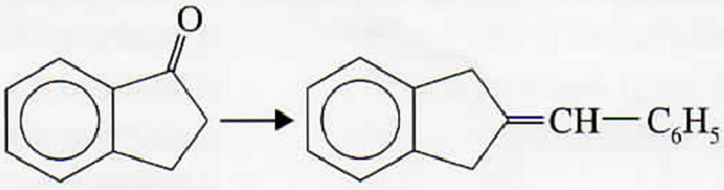
$C_6H_5CHO \longrightarrow C_6H_5CH_2\underset{\overset{|}{CH_3}}{C}HNH_2$

(d) 

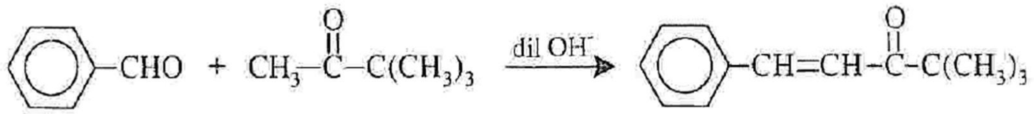
(e) 

(f) 

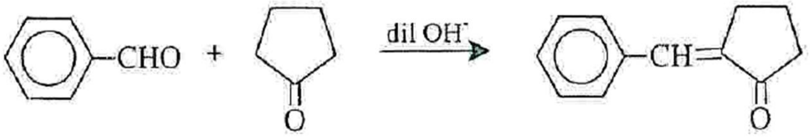
$CH_3CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}H \longrightarrow CH_3(CH_2)_3CH{=}\overset{\overset{CH_2OH}{|}}{C}(CH_2)_2CH_3$

(g) 

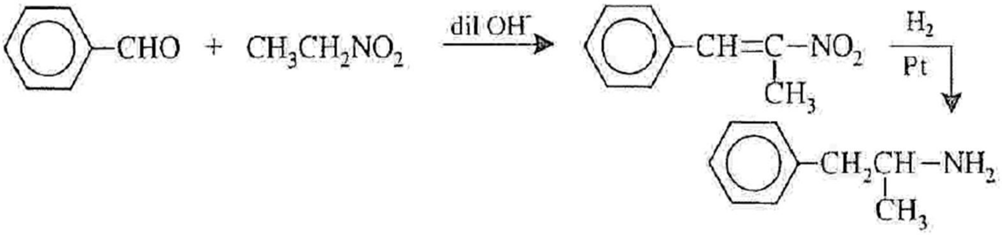
17.31 (a)



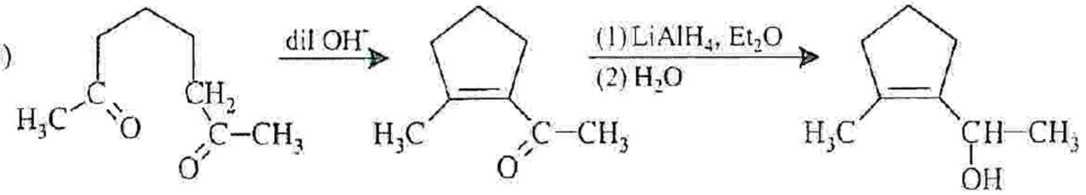
(b)



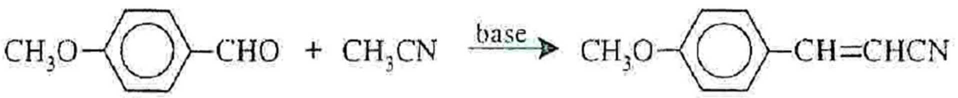
(c)



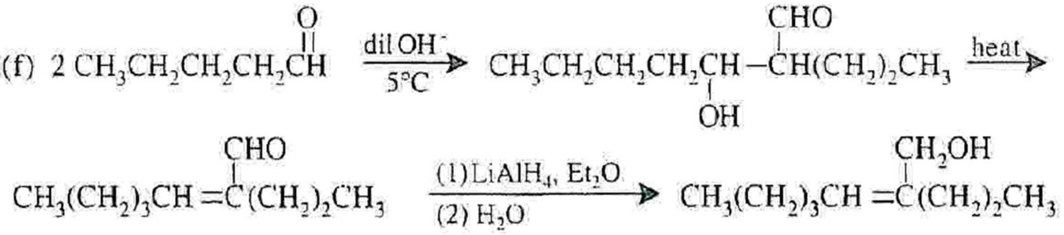
(d)



(e)



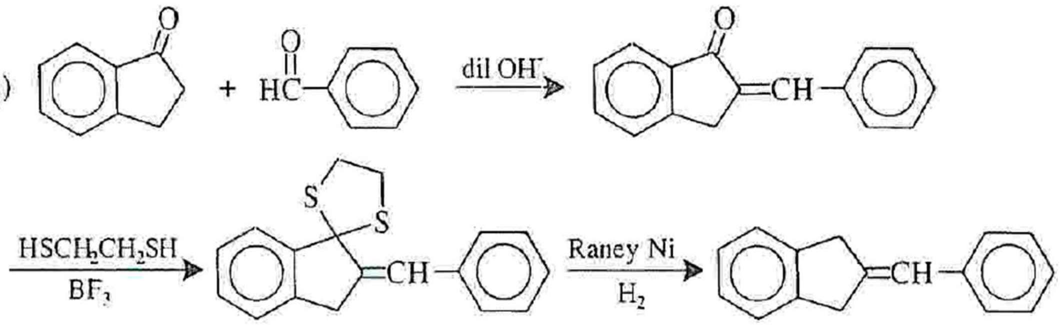
(f)



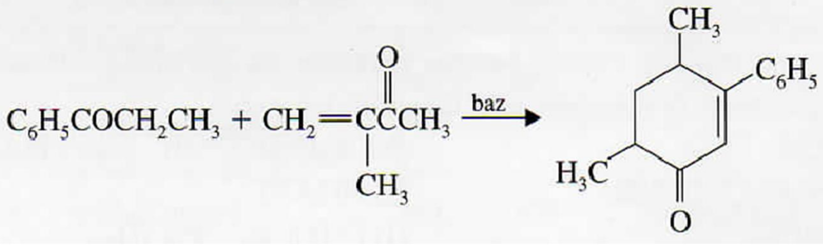
$$2\,CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}H \xrightarrow[5°C]{dil\,OH^-} CH_3CH_2CH_2CH_2\underset{OH}{CH}-\overset{CHO}{C}H(CH_2)_2CH_3 \xrightarrow{heat}$$

$$CH_3(CH_2)_3CH=\overset{CHO}{C}(CH_2)_2CH_3 \xrightarrow[(2)\,H_2O]{(1)\,LiAlH_4,\,Et_2O} CH_3(CH_2)_3CH=\overset{CH_2OH}{C}(CH_2)_2CH_3$$

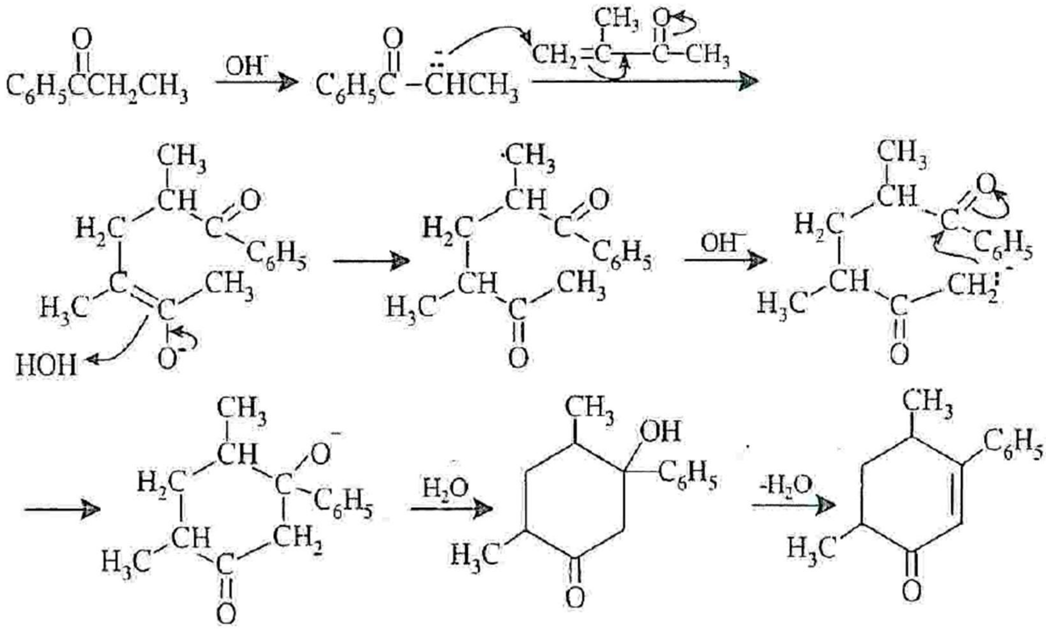
(g)



17.32 Aşağıdaki tepkime Robinson halkalama tepkimesini (Altbölüm 17.9B) gösterir. Her bir basamağın mekanizmasını gösteriniz.



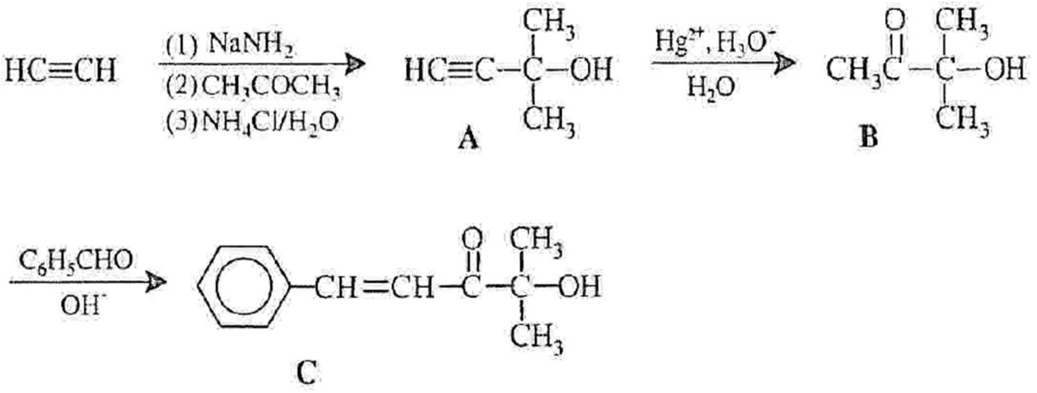
17.32



17.33 A, B ve C için yapı formüllerini yazınız.

$$HC\equiv CH \xrightarrow[\substack{(2)\ CH_3COCH_3\\(3)\ NH_4Cl/H_2O}]{(1)\ NaNH_2,\ \text{sıvı}\ NH_3} \mathbf{A}\ (C_5H_8O) \xrightarrow[H_2O]{Hg^{2+},\ H_3O^+} \mathbf{B}\ (C_5H_{10}O_2) \xrightarrow{C_6H_5CHO,\ OH^-} \mathbf{C}\ (C_{12}H_{14}O_2)$$

17.33



17.34 Krotonaldehitin γ karbonunun hidrojen atomları oldukça asidiktir ($pK_a \cong 20$).

$$\overset{\gamma}{C}H_3\,\overset{\beta}{C}H{=}\overset{\alpha}{C}HCHO$$

Krotonaldehit

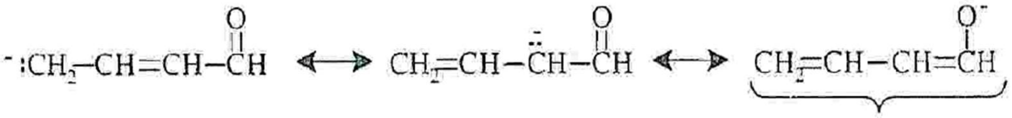
(a) Bu durumu açıklayacak rezonans yapıları yazınız.

(b) Aşağıdaki tepkimeyi açıklayan bir mekanizma yazınız.

$$C_6H_5CH{=}CHCHO + CH_3CH{=}CHCHO \xrightarrow[EtOH]{baz} C_6H_5(CH{=}CH)_3CHO$$

(%87)

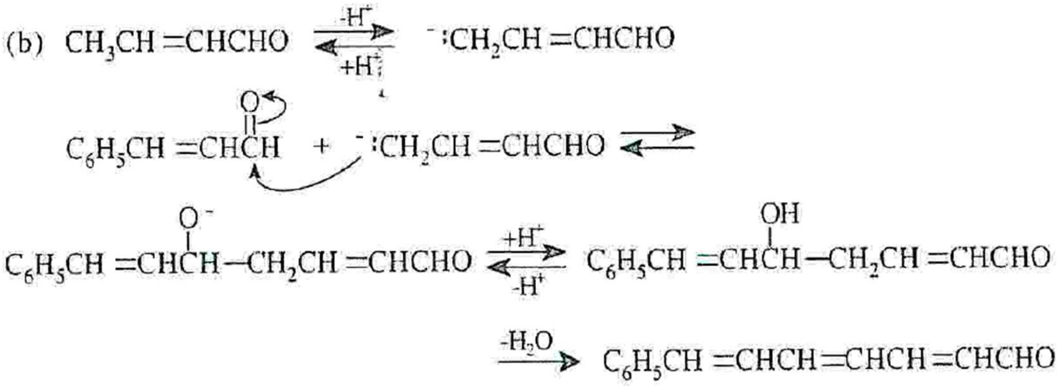
17.34 (a) The conjugate base is a hybrid of the following structures:



$$^{-}\!:CH_2-CH=CH-\overset{\overset{O}{\|}}{C}H \longleftrightarrow CH_2=CH-\overset{-}{\ddot{C}}H-\overset{\overset{O}{\|}}{C}H \longleftrightarrow \underbrace{CH_2=CH-CH=\overset{\overset{O^-}{|}}{C}H}$$

This structure is especially stable because the negative charge is on the oxygen atom.

(b)



$$CH_3CH=CHCHO \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} {}^{-}\!:CH_2CH=CHCHO$$

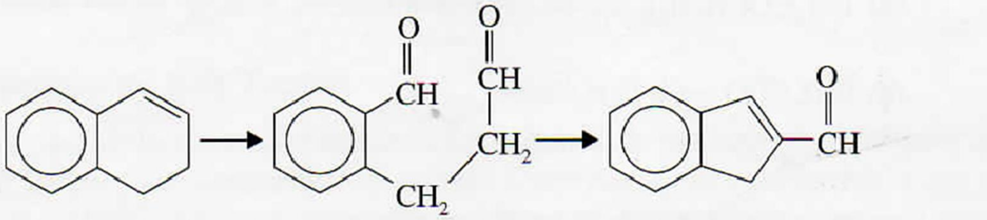
$$C_6H_5CH=CH\overset{\overset{O}{\|}}{C}H + {}^{-}\!:CH_2CH=CHCHO \rightleftharpoons$$

$$C_6H_5CH=CH\overset{\overset{O^-}{|}}{C}H-CH_2CH=CHCHO \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} C_6H_5CH=CH\overset{\overset{OH}{|}}{C}H-CH_2CH=CHCHO$$

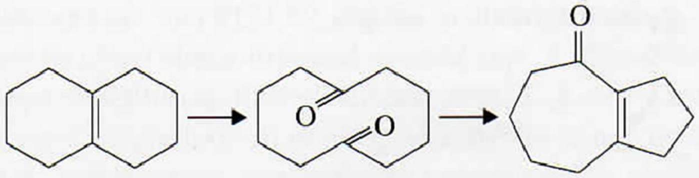
$$\xrightarrow{-H_2O} C_6H_5CH=CHCH=CHCH=CHCHO$$

17.35 Aşağıdaki sentezin her bir basamağını gerçekleştirmek için hangi reaktifleri kullanırdınız?

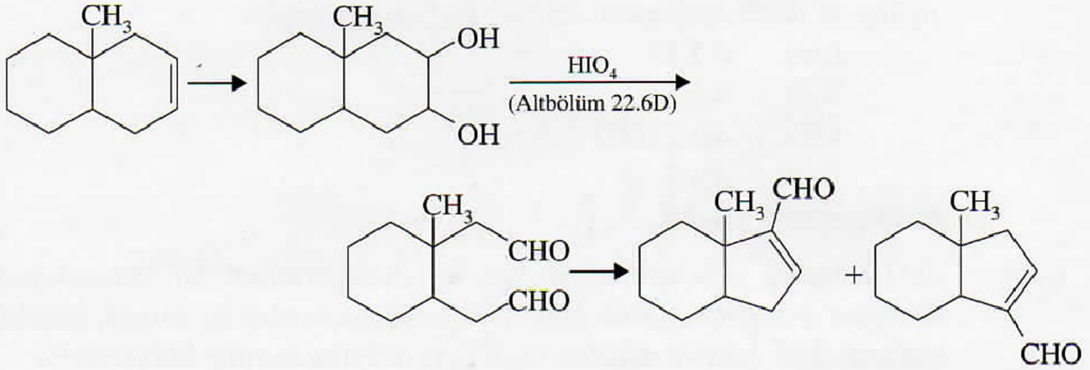
(a)



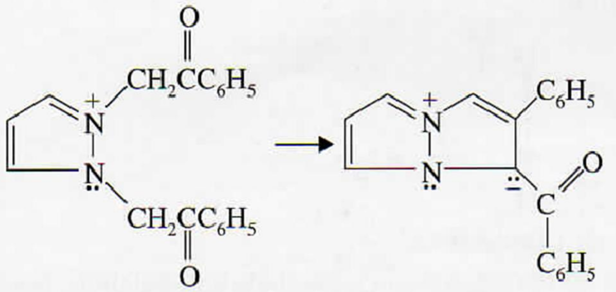
(b)



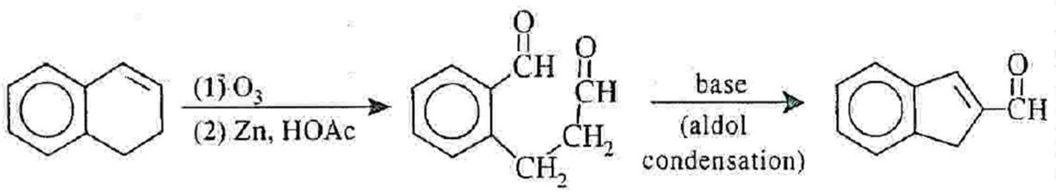
(c)



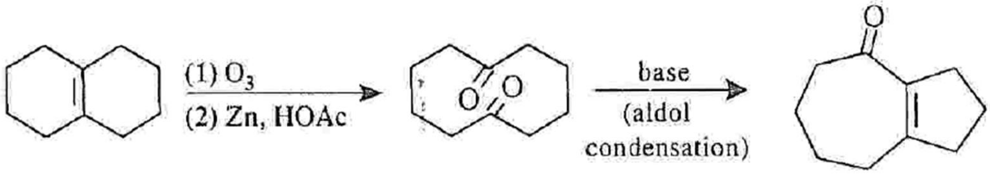
(d)



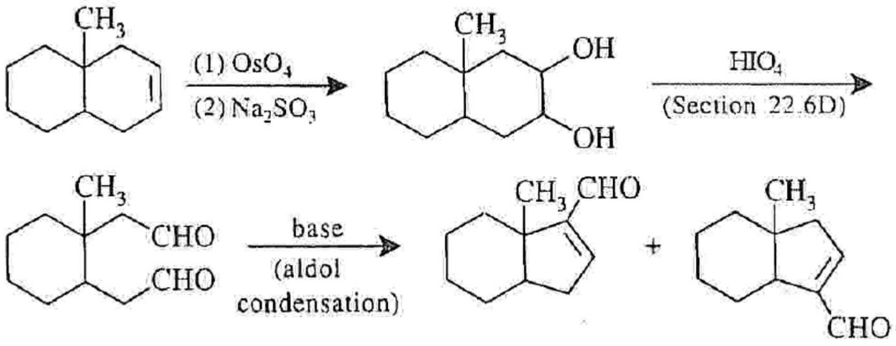
17.35 (a)



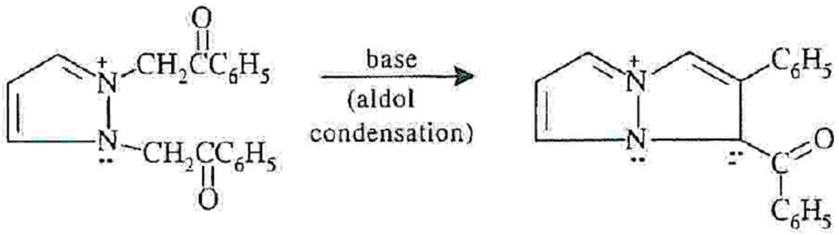
(b)



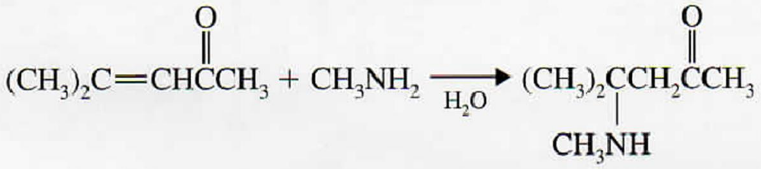
(c)



(d)



17.36 **(a)** İnfrared spektrokopisi, bir Grignard bileşiğinin, bir α,β-doymamış ketona katılma ürününün basit katılma ürünü mü ya da konjuge katılma ürünü mü olduğuna karar vermek için basit bir yöntem sağlar. Açıklayınız. (Hangi pik veya pikler araştırılmalıdır?). **(b)** UV spektroskopi kullanarak aşağıdaki tepkimenin hızını nasıl takip edebilirsiniz?



$$(CH_3)_2C{=}CH\overset{O}{\overset{\|}{C}}CH_3 + CH_3NH_2 \xrightarrow[H_2O]{} (CH_3)_2\underset{CH_3NH}{\underset{|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3$$

17.36 (a) In simple addition, the carbonyl peak (1665–1780-cm^{-1} region) does not appear in the product; in conjugate addition it does.

(b) As the reaction takes place, the long-wavelength absorption arising from the conjugated system should disappear. One could follow the rate of the reaction by following the rate at which this absorption peak disappears.

17.37 **(a)** **U**($C_9H_{10}O$) bileşiği olumsuz iyodoform testi vermektedir. **U**'nun İR spektrumu 1690 cm^{-1} de kuvvetli bir soğurma piki gösterir. **U**'nun ^1H NMR spektrumu verileri ise aşağıda verilmiştir.

Üçlü	δ 1,2 (3H)
Dörtlü	δ 3,0 (2H)
Çoklu	δ 7,7 (5H)

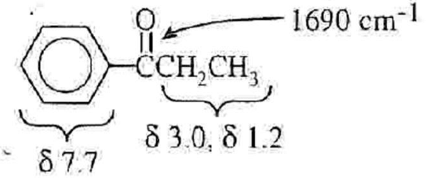
U'nun yapısını bulunuz.

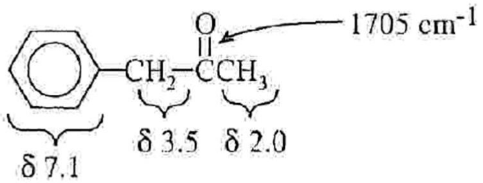
(b) **V** bileşiği, **U**'nun bir izomeridir. **V** bileşiği olumlu iyodoform testi veriyor. **V**'nin İR spektrumu 1705 cm^{-1} de kuvvetli bir pik gösteriyor. **V**'nin ^1H NMR spektrumu verileri aşağıda verilmiştir:

Birli	δ 2,0 (3H)
Birli	δ 3,5 (2H)
Çoklu	δ 7,1 (5H)

V'nin yapısını bulunuz.

17.37 (a) Compound **U** is ethyl phenyl ketone: (b) Compound **V** is benzyl methyl ketone:

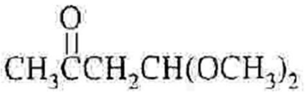


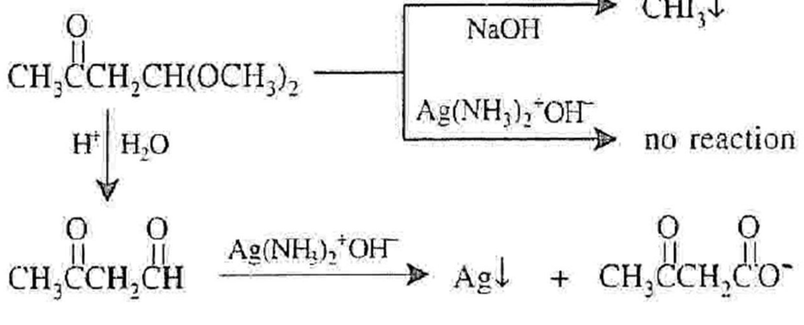


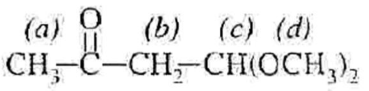
17.38 **A** bileşiği $C_6H_{12}O_3$ molekül formülüne sahiptir ve 1710 cm^{-1} de kuvvetli İR soğurma piki göstermektedir. **A,** sulu sodyum hidroksit içinde iyotla etkileştirildiğinde sarı çökelek verir. **A,** Tollens reaktifi ile etkileştirildiğinde tepkime olmaz, fakat **A** önce bir damla sülfirik asit içeren su ile etkileştirilir sonra Tollens reaktifi ile muamele edilirse deney tüpünde gümüş aynası oluşur. **A** bileşiğinin ^1H NMR spektrumu verileri aşağıda verilmiştir:

Birli	δ 2,1
İkili	δ 2,6
Birli	δ 3,2 (6H)
Üçlü	δ 4,7

A'nın yapısını yazınız.

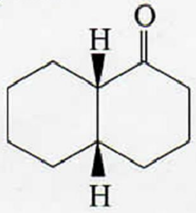
17.38 **A** is  $CH_3\overset{O}{\overset{||}{C}}CH_2CH(OCH_3)_2$




$$\overset{(a)}{CH_3}-\overset{O}{\overset{||}{C}}-\overset{(b)}{CH_2}-\overset{(c)}{CH}\overset{(d)}{(OCH_3)_2}$$

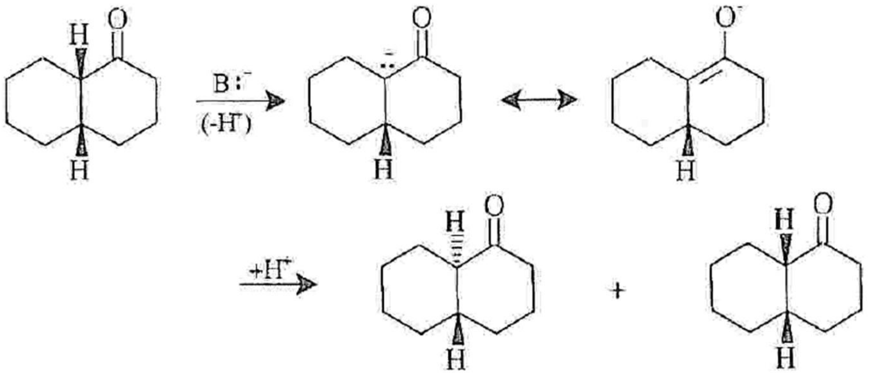
(a) Singlet δ 2.1
(b) Doublet δ 2.6
(c) Triplet δ 4.7
(d) Singlet δ 3.2

17.39 *cis*-1-Dekalon çözeltisinin bir baz ile etkileştirilmesi bir izomerleşmenin meydana gelmesine neden olur. Sistem dengeye ulaştığı zaman, çözeltinin, yaklaşık %95 *trans*-1-dekalon ve %5 *cis*-dekalon içerdiği bulunmuştur. Bu izomerleşmeyi açıklayınız.



***cis*-1-Dekalon**

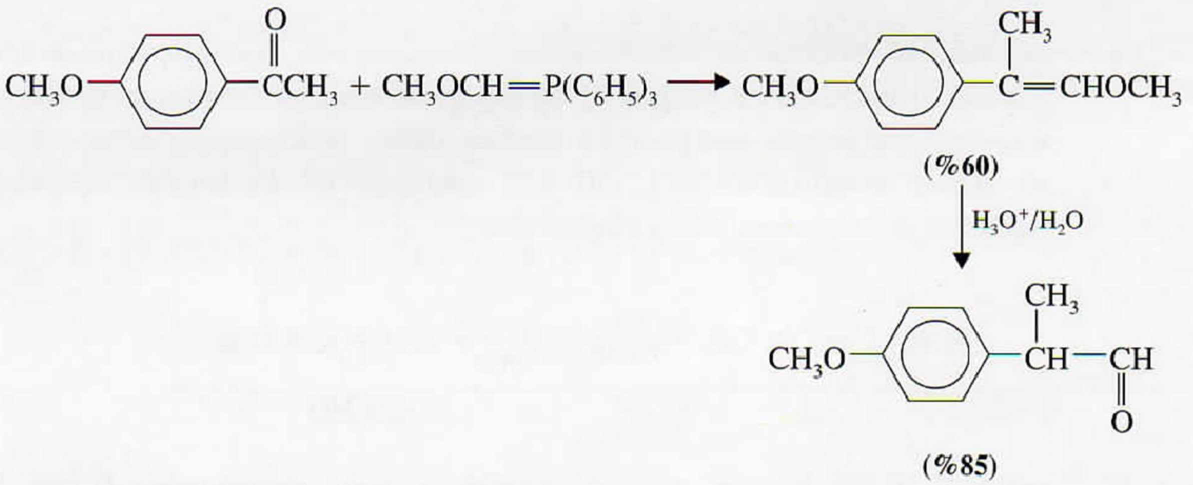
17.39 Abstraction of an *α* hydrogen at the ring junction yields an enolate ion that can then accept a proton to form either *trans*-1-decalone or *cis*-1-decalone. Since *trans*-1-decalone is more stable, it predominates at equilibrium.

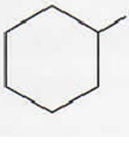


(95%)
trans-1-Decalone
(more stable)

(5%)
cis-1-Decalone
(less stable)

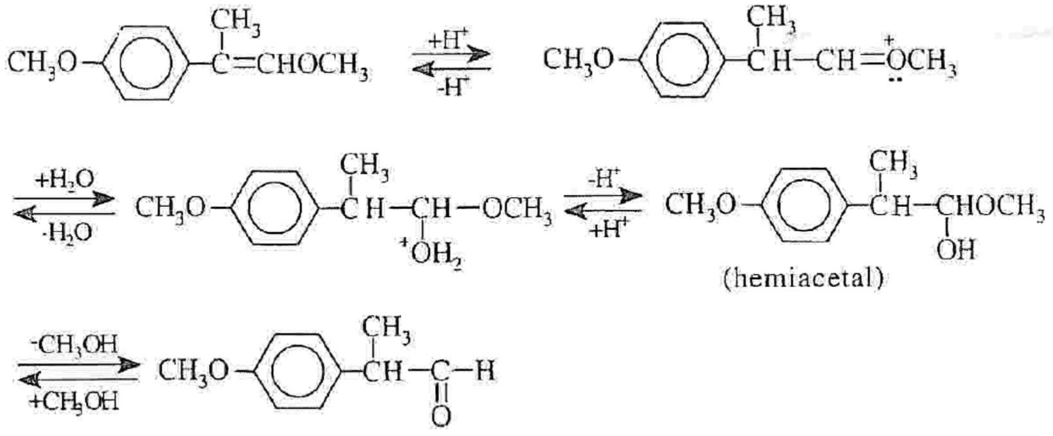
17.40 Wittig tepkimesi (Altbölüm 16.10) aldehitlerin sentezinde kullanılabilir, örneğin.



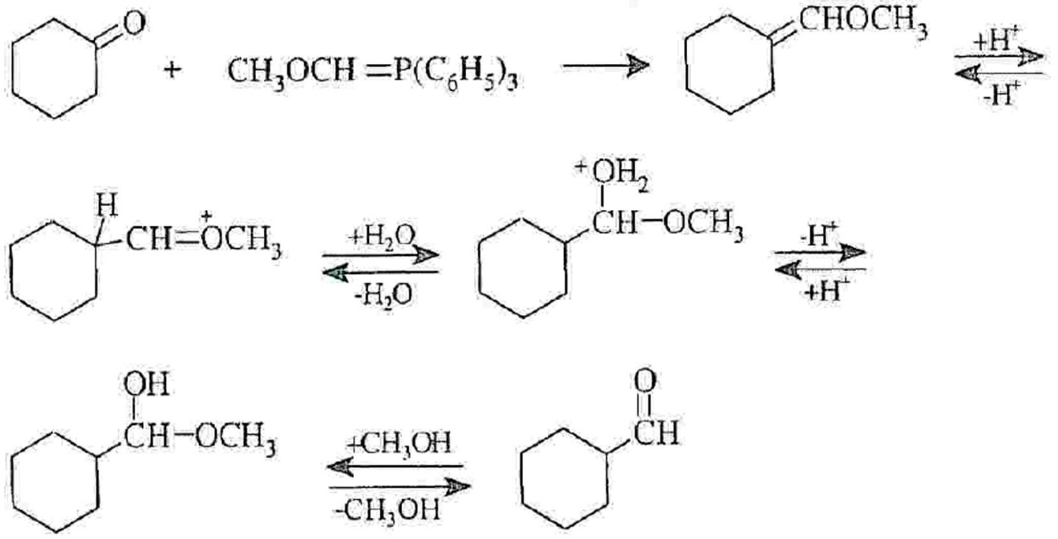
(a) $CH_3OCH{=}P(C_6H_5)_3$ bileşiğini nasıl hazırlardınız? **(b)** İkinci tepkimenin aldehiti nasıl oluşturduğunu bir mekanizma ile gösteriniz.
(c) Sikloheksanondan  CHO bileşiğinin hazırlanmasında bu yöntemi nasıl kullanırdınız?

17.40 (a) $CH_3OCH_2Br + (C_6H_5)_3P \xrightarrow{(2)\ RLi} CH_3OCH{=}P(C_6H_5)_3$

(b) Hydrolysis of the ether yields a hemiacetal that then goes on to form an aldehyde.



(c)

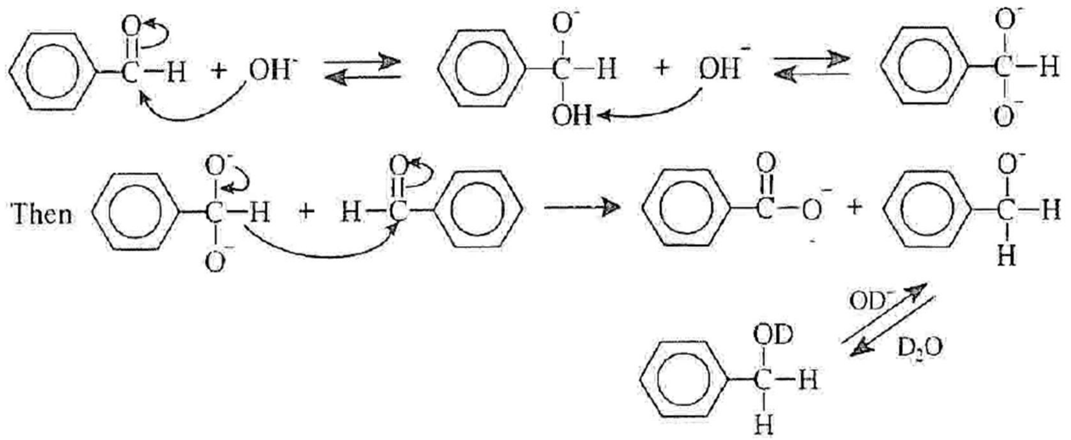


17.41 α-Hidrojeni içermeyen aldehitler, derişik baz ile etkileştirildiğinde **Cannizzaro tepkimesi** olarak anılan bir moleküller arası yükseltgenme–indirgenmeye uğrarlar. Buna bir örnek, benzaldehitin aşağıdaki tepkimesidir.

$$2\,C_6H_5{-}CHO \xrightarrow[H_2O]{OH^-} C_6H_5{-}CH_2OH + C_6H_5{-}CO_2^-$$

(a) Tepkime D_2O içerisinde yapılırsa, ayrılan benzil alkol, karbon atomuna bağlı döteryum içermez. Ürün $C_6H_5CH_2OD$'dir. Bu sonuç tepkime mekanizması açısından size ne ifade ediyor? **(b)** $(CH_3)_2CHCHO$ ve $Ba(OH)_2/H_2O$ kapalı bir tüpte ısıtılırsa tepkimede yalnız $(CH_3)_2CHCH_2OH$ ve $[(CH_3)_2CHCO_2]_2$ Ba oluşur. Aldol tepkimesinden beklenenler yerine bu ürünlerin oluşumunu nasıl açıklarsınız?

17.41 (a) The hydrogen atom that is added to the aldehyde carbon atom in the reduction must come from the other aldehyde rather than from the solvent. It must be transferred as a hydride ion and directly from molecule to molecule, since if it were ever a free species it would react immediately with the solvent. A possible mechanism is the following:



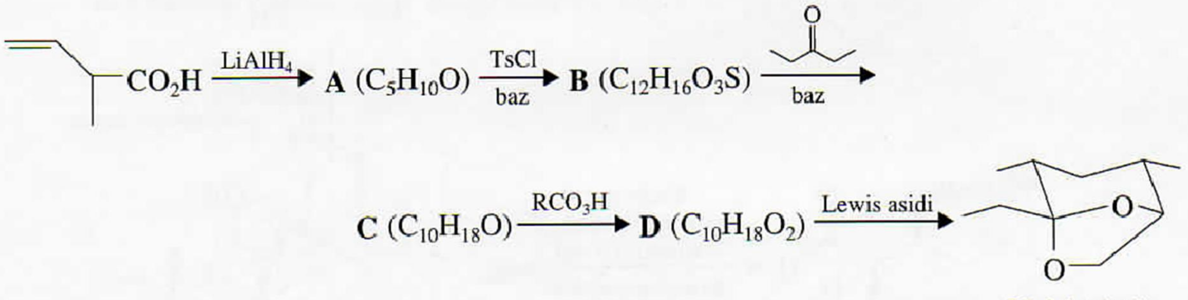
(b) Although an aldol reaction occurs initially, the aldol reaction is reversible. The Cannizzaro reaction, though slower, is irreversible. Eventually, all the product is in the form of the alcohol and the carboxylate ion.

17.42 **Asetaldehitin aldol tepkimesi D_2O içerisinde yapılırsa, tepkimeye girmemiş aldehitin metil grubunda döteryum bulunmaz. Fakat, asetonun aldol tepkimesinde, tepkimeye girmemiş asetonun metil grubuna döteryum bağlanmıştır. Bu farklı davranışı açıklayınız.**

17.42 This difference in behavior indicates that, for acetaldehyde, the capture of a proton from the solvent (the reverse of the reaction by which the enolate ion is formed) occurs much more slowly than the attack by the enolate ion on another molecule.

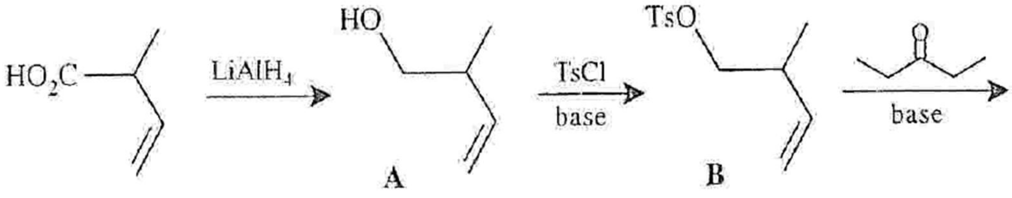
When acetone is used, the equilibrium for the formation of the enolate ion is unfavorable, but more importantly, enolate attack on another acetone molecule is disfavored due to steric hindrance. Here proton capture (actually deuteron capture) competes very well with the aldol reaction.

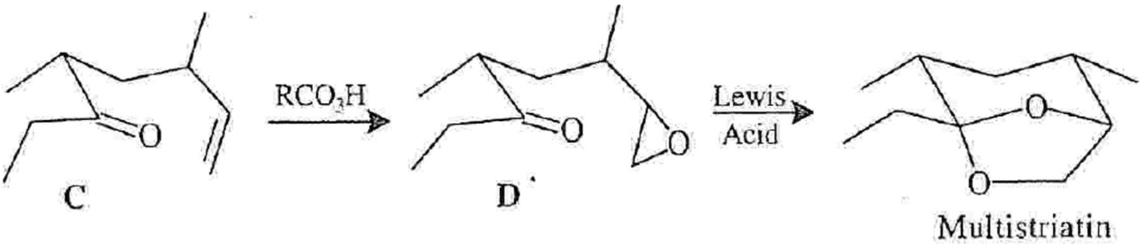
17.43 **Aşağıda, karaağaç kabuk böceğinin feromonu olan multistriatinin (bkz. Problem 16.46) sentezi görülmektedir. A, B, C ve D bileşiklerinin yapılarını yazınız.**



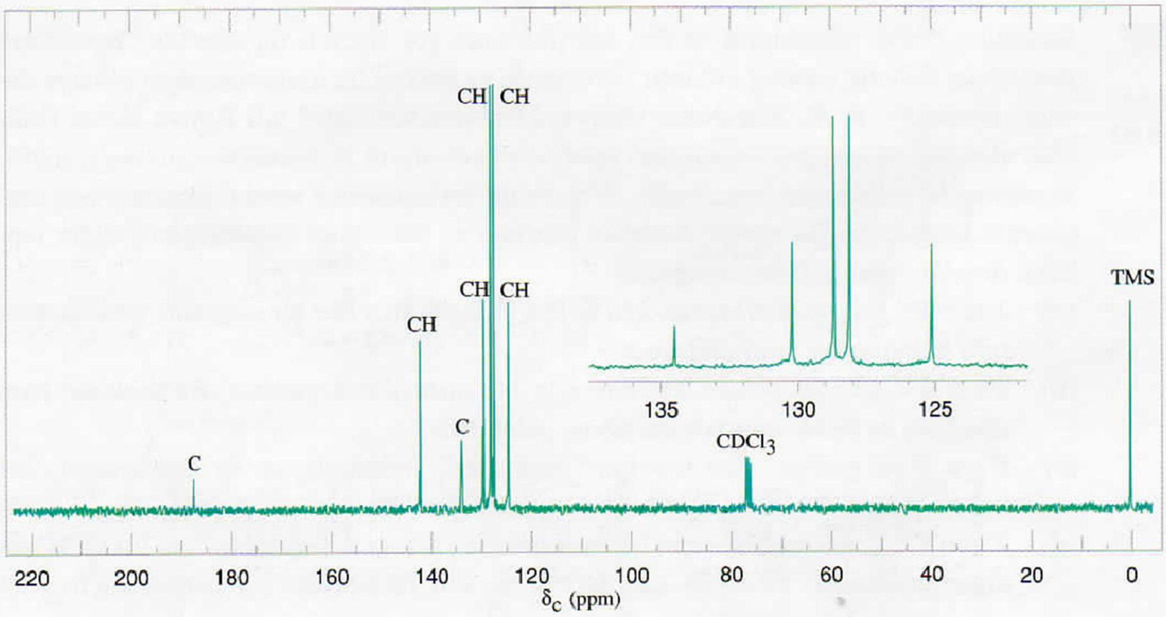
Multistriatin

17.43

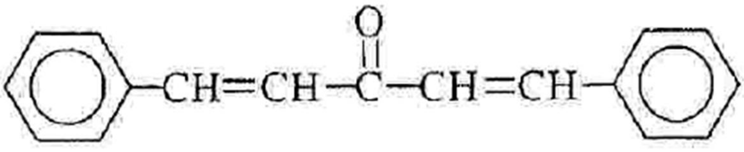




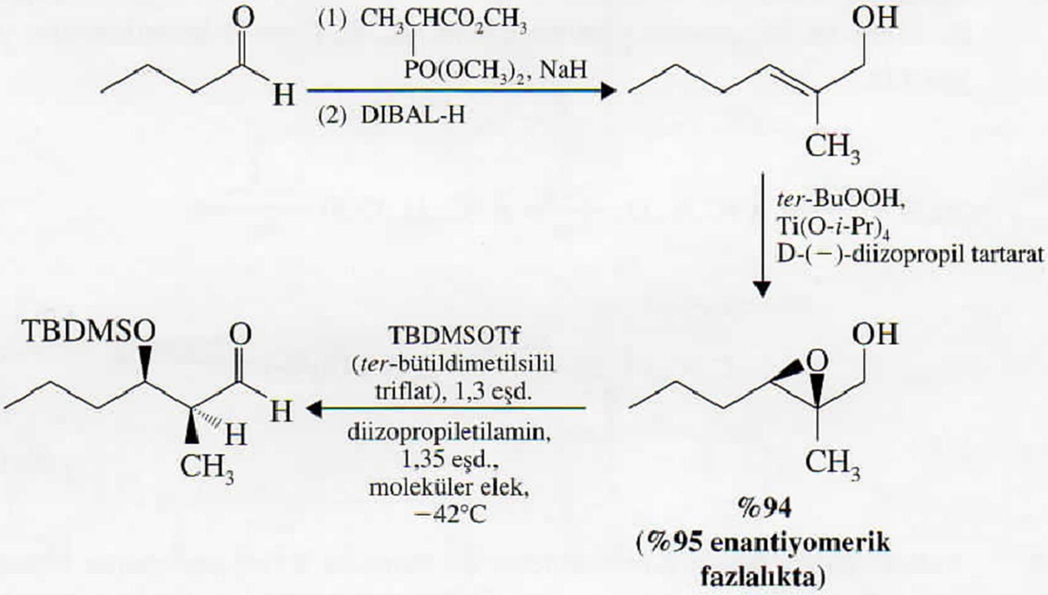
17.44 Aseton 2 eşdeğer mol benzaldehit ile etonollü KOH varlığında tepkimeye girerse **X** bileşiği meydana gelir. **X**'in ^{13}C NMR spektrumu Şekil 17.2'de verilmiştir. **X** bileşiği için bir yapı öneriniz.



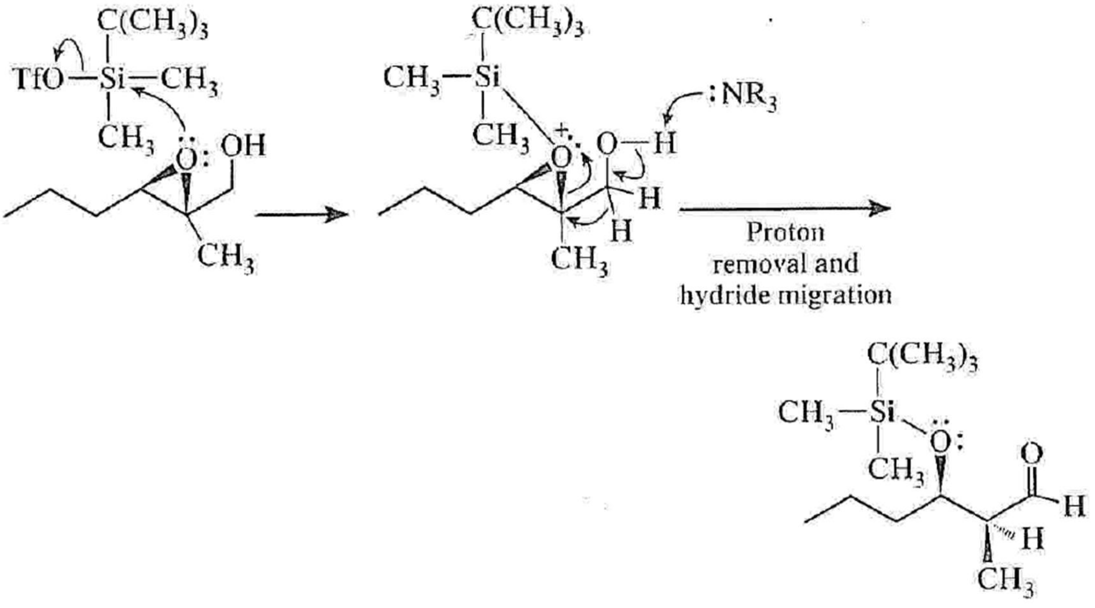
Şekil 17.2 X bileşiğinin genişband proton–eşleşmesiz ^{13}C NMR spektrumu (Problem 17.44). DEPT ^{13}C NMR spektrumlardan elde edilen bilgiler piklerin üstünde verilmektedir.

17.44 **X** is: 

***17.45** Aldol tepkimesi olmamasına karşın, aldol katılma ürünlerinin enantiyoözgü oluşumuyla sonuçlanan, Derin C. D'Amico ve Michael E. Jung (UCLA) tarafından geliştirilen bir tepkimenin basamaklarına bir örnek aşağıda verilmiştir. Basamaklar, Horner–Wadsworth–Emmons tepkimesi (Altbölüm 16.10), Sharpless asimetrik epoksitleme (Altbölüm 11.17), ve sonunda aldol tipi ürünler veren özel çevrilmeler içerir. Gösterilen deney şartlarında, epoksi alkolün çevrilerek aldol ürünleri oluşturması için bir mekanizma öneriniz. [*İpucu:* Çevrilme, önce epoksi alkolden bir trialkilsilil eterin ayrı bir tepkimeyle hazırlanması ve sonra, oluşan silil eterin bir Lewis asit katalizörü (örneğin BF_3) ile etkileştirilmesiyle de gerçekleştirilebilir.]

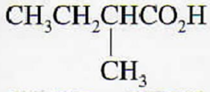

O
H
(1) $CH_3CHCO_2CH_3$
$PO(OCH_3)_2$, NaH
(2) DIBAL-H
OH
CH_3
ter-BuOOH,
$Ti(O\text{-}i\text{-}Pr)_4$
D-(−)-diizopropil tartarat
TBDMSO
O
H
CH_3
TBDMSOTf
(ter-bütildimetilsilil triflat), 1,3 eşd.
diizopropiletilamin, 1,35 eşd., moleküler elek, −42°C
OH
O
CH_3
%94
(%95 enantiyomerik fazlalıkta)

*17.45



Karboksilik Asitler ve Türevleri. Açil Karbonunda Nükleofilik Katılma-Ayrılma

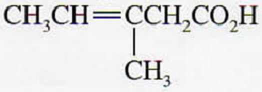
Problem 18.1 Aşağıdaki her bir maddenin adını IUPAC sistematik adlandırmasına göre yazınız:

(a) 
$CH_3CH_2\underset{CH_3}{C}HCO_2H$

(b) $CH_3CH{=}CHCH_2CO_2H$

(c) $BrCH_2CH_2CH_2CO_2Na$

(d) $C_6H_5CH_2CH_2CH_2CH_2CO_2H$

(e) 
$CH_3CH{=}\underset{CH_3}{C}CH_2CO_2H$

18.1 (a) 2-Methylbutanoic acid

(b) 3-Pentenoic acid

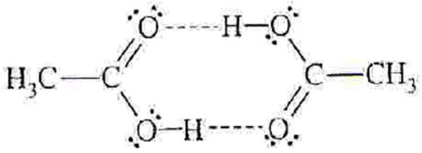
(c) Sodium 4-bromobutanoate

(d) 5-Phenylpentanoic acid

(e) 3-Methyl-3-pentenoic acid

Problem 18.2 Bir deneyde asetik asitin buhar fazındaki (kaynama noktasının hemen üstünde) molekül kütlesinin yaklaşık olarak 120 olduğu bulunmuştur. Bu deneysel değerle yaklaşık 60 olan gerçek değer arasındaki farklılığı açıklayınız.

18.2 Acetic acid, in the absence of solvating molecules, exists as a dimer owing to the formation of two intermolecular hydrogen bonds:



At temperatures much above the boiling point, the dimer dissociates into the individual molecules.

Problem 18.3 Aşağıdaki her bir asit çiftinden hangisi daha kuvvetlidir?

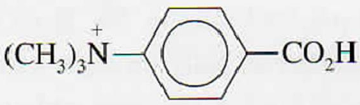
(a) CH_3CO_2H veya CH_2FCO_2H

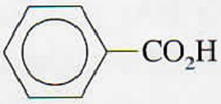
(b) CH_2FCO_2H veya CH_2ClCO_2H

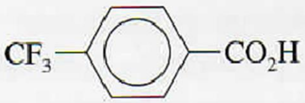
(c) CH_2ClCO_2H veya CH_2BrCO_2H

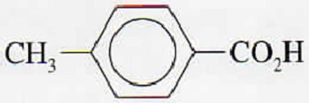
(d) $CH_2FCH_2CH_2CO_2H$ veya $CH_3CHFCH_2CO_2H$

(e) $CH_3CH_2CHFCO_2H$ veya $CH_3CHFCH_2CO_2H$

(f) 

veya 

(g) 

veya 

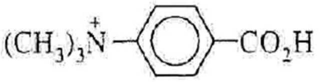
18.3 (a) CH_2FCO_2H (F– is more electronegative than H-)

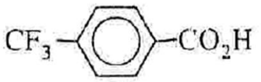
(b) CH_2FCO_2H (F– is more electronegative than Cl-)

(c) CH_2ClCO_2H (Cl– is more electronegative than Br-)

(d) $CH_3CHFCH_2CO_2H$ (F– is closer to $-CO_2H$)

(e) $CH_3CH_2CHFCO_2H$ (F– is closer to $-CO_2H$)

(f) 
$[(CH_3)_3\overset{+}{N}$- is more electronegative than H-]

(g) 
(CF_3– is more electronegative than CH_3-)

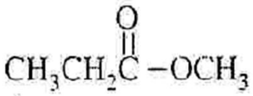
Problem 18.4 ➤ Aşağıdaki gerçekler için bir açıklama getiriniz. (a) Dikarboksilik asitlerin hepsinin pK_1 değerleri aynı sayıda karbon atomu içeren monokarboksilik asitlerin pK_a değerlerinden daha küçüktür. (b) $HO_2C(CH_2)_nCO_2H$ türü dikarboksilik asitlerini pK_1 ve pK_2 değerleri arasındaki fark n arttıkça azalır.

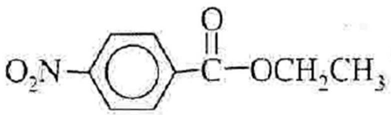
18.4 (a) The carboxyl group is an electron-withdrawing group; thus, in a dicarboxylic acid such as those in Table 18.3, one carboxyl group increases the acidity of the other.

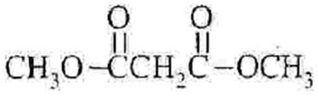
(b) As the distance between the carboxyl groups increases the acid-strengthening, inductive effect decreases.

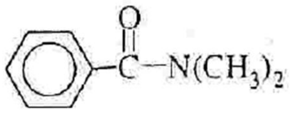
Problem 18.5 ◄ Aşağıdakilerin yapı formüllerini yazınız.

(a) Metil propanoat	**(f)** Dimetil ftalat
(b) Etil *p*-nitrobenzoat	**(g)** Dipropil maleat
(c) Dimetil malonat	**(h)** *N,N*-Dimetilformamit
(d) *N,N*-Dimetilbenzamit	**(i)** 2-Bromopropanoil bromür
(e) Pentannitril	**(j)** Dietil süksinat

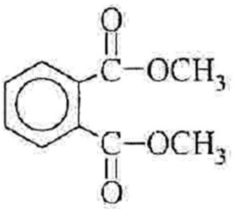
18.5 (a) 
$CH_3CH_2\overset{O}{\overset{\|}{C}}-OCH_3$

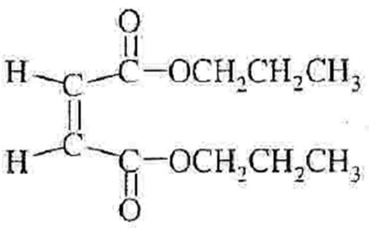
(b) 

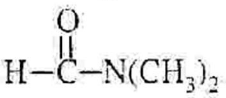
(c) 
$CH_3O-\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}-OCH_3$

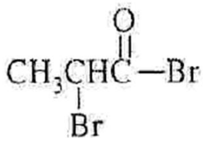
(d) 

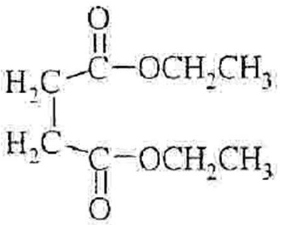
(e) $CH_3CH_2CH_2CH_2C{\equiv}N$

(f) 

(g) 

(h) 
$H-\overset{O}{\overset{\|}{C}}-N(CH_3)_2$

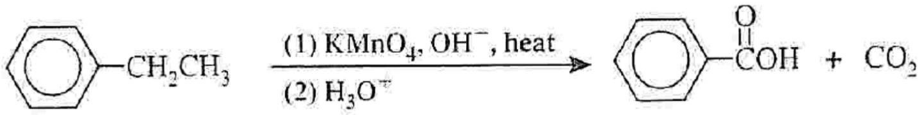
(i) 
$CH_3\underset{Br}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}-Br$

(j) 

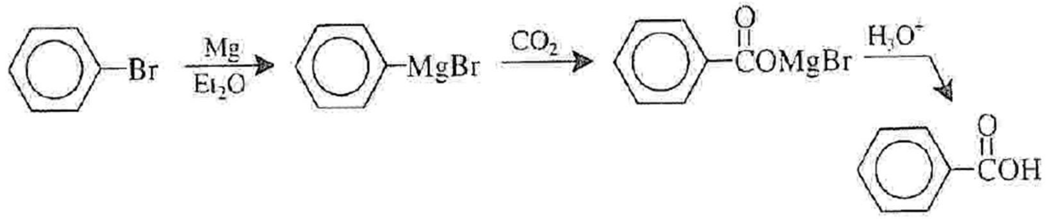
Problem 18.6 ➤ Aşağıdaki her bir madde benzoik asite nasıl dönüştürülebilir? Gösteriniz.

(a) Etilbenzen	**(c)** Asetofenon	**(e)** Benzil alkol
(b) Bromobenzen	**(d)** Fenileten (stiren)	**(f)** Benzaldehit

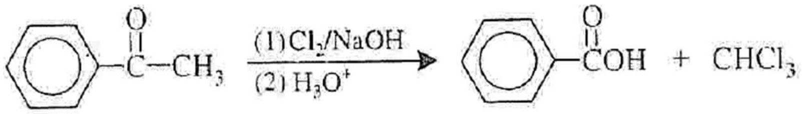
18.6 (a)



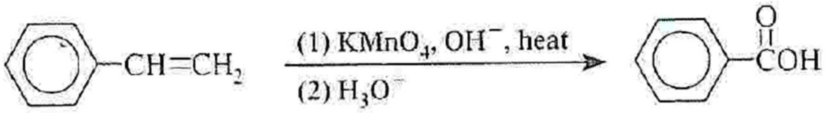
(b)



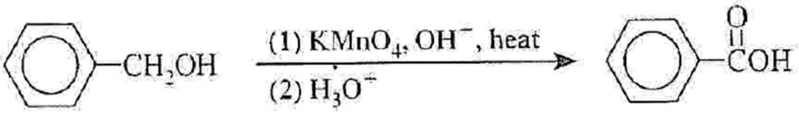
(c)



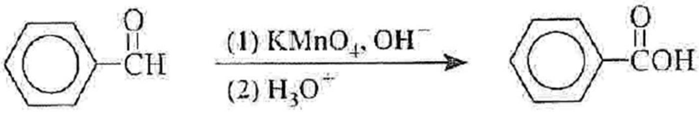
(d)



(e)



(f)

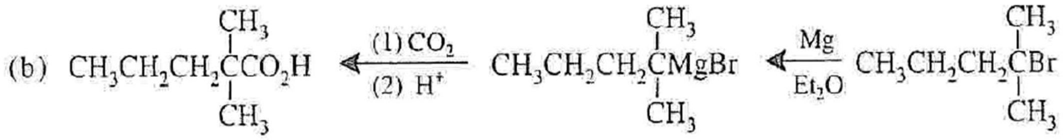


Problem 18.7 ➤ Aşağıdaki her bir karboksilik asidin Grignard sentezi üzerinden nasıl elde edilebileceğini gösteriniz.

(a) Fenilasetik asit	**(c)** 3-Bütenoik asit	**(e)** Heksanoik asit
(b) 2,2-Dimetilpentanoik asit	**(d)** 4-Metilbenzoik asit	

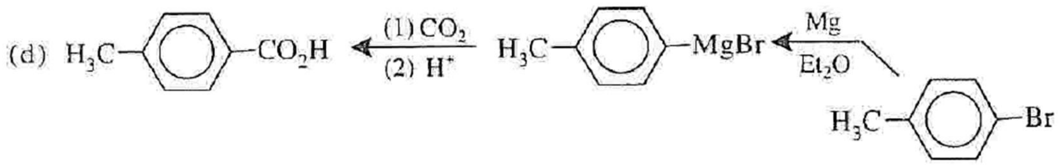
18.7 These syntheses are easy to see if we work backward.

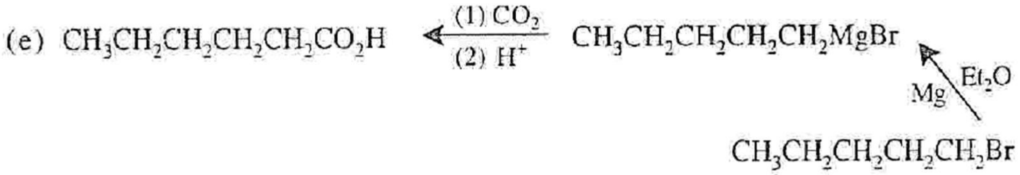
(a) $C_6H_5CH_2CO_2H \xleftarrow[(2)\ H^+]{(1)\ CO_2} C_6H_5CH_2MgBr \xleftarrow[Et_2O]{Mg} C_6H_5CH_2Br$



(b) $CH_3CH_2CH_2C(CH_3)_2CO_2H \xleftarrow[(2)\ H^+]{(1)\ CO_2} CH_3CH_2CH_2C(CH_3)_2MgBr \xleftarrow[Et_2O]{Mg} CH_3CH_2CH_2C(CH_3)_2Br$

(c) $CH_2{=}CHCH_2CO_2H \xleftarrow[(2)\ H^+]{(1)\ CO_2} CH_2{=}CHCH_2MgBr \xleftarrow[Et_2O]{Mg} CH_2{=}CHCH_2Br$





(e) $CH_3CH_2CH_2CH_2CH_2CO_2H \xleftarrow[(2)\ H^+]{(1)\ CO_2} CH_3CH_2CH_2CH_2CH_2MgBr \xleftarrow[Et_2O]{Mg} CH_3CH_2CH_2CH_2CH_2Br$

Problem 18.8 ➤ (**a**) Problem 18.7'deki karboksilik asitlerden hangisi nitril sentezi yardımıyla hazırlanabilir? (**b**) $HOCH_2CH_2CH_2CH_2Br$ den $HOCH_2CH_2CH_2CH_2CO_2H$ elde etmek için Grignard veya nitril sentez yöntemlerinden hangisini seçersiniz? Niçin?

18.8 (a) $C_6H_5CH_2CO_2H \xleftarrow[(2)\ H^+,\ H_2O,\ heat]{(1)\ CN^-} C_6H_5CH_2Br$

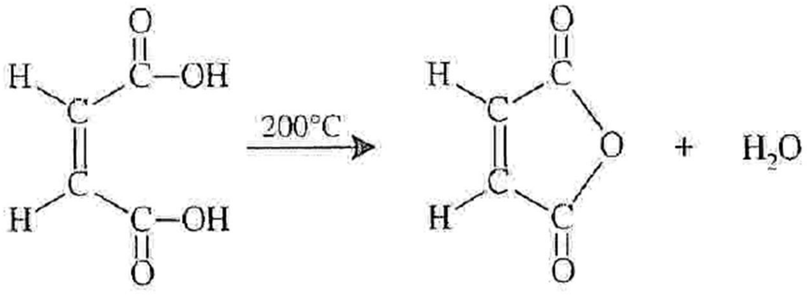
$CH_2{=}CHCH_2CO_2H \xleftarrow[(2)\ H^+,\ H_2O,\ heat]{(1)\ CN^-} CH_2{=}CHCH_2Br$

$CH_3CH_2CH_2CH_2CH_2CO_2H \xleftarrow[(2)\ H^+,\ H_2O,\ heat]{(1)\ CN^-} CH_3CH_2CH_2CH_2CH_2Br$

(b) A nitrile synthesis. Preparation of a Grignard reagent from $HOCH_2CH_2CH_2CH_2Br$ would not be possible because of the presence of the acidic hydroxyl group.

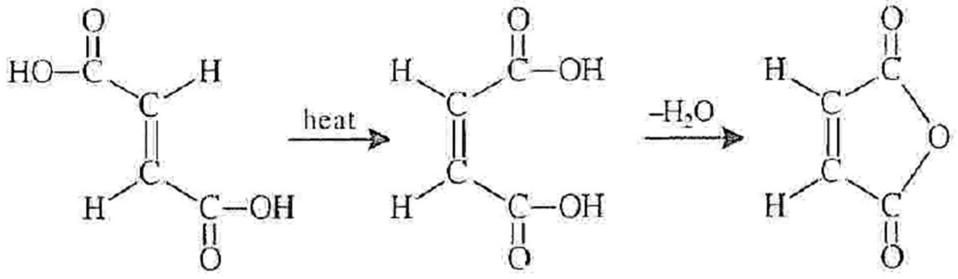
Problem 18.9 ➤ Maleik asit 200°C'a ısıtıldığı zaman su kaybederek maleik anhidrit oluşur. Fumarik asit maleik asitin diastereomeridir ve su kaybetmesi için daha yüksek sıcaklık gerekir. Fumarik asit daha yüksek sıcaklıkta ısıtıldığında maleik anhidrit oluşur. Bu gözlemler için bir açıklama yapınız.

18.9 Since maleic acid is a cis dicarboxylic acid, dehydration occurs readily:



Maleic acid   Maleic anhydride

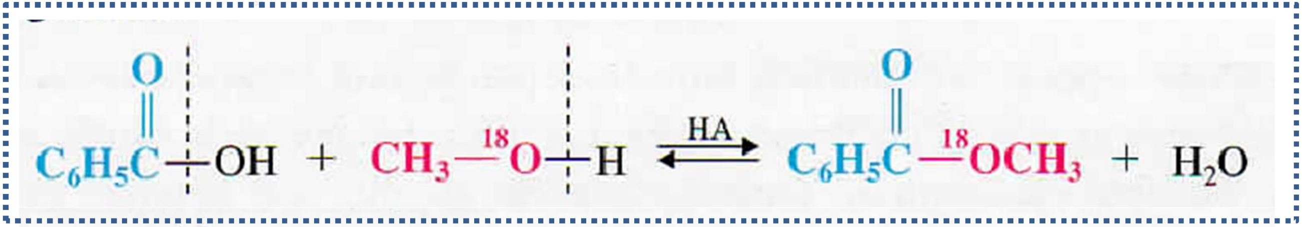
Being a trans dicarboxylic acid, fumaric acid must undergo isomerization to maleic acid first. This isomerization requires a higher temperature.



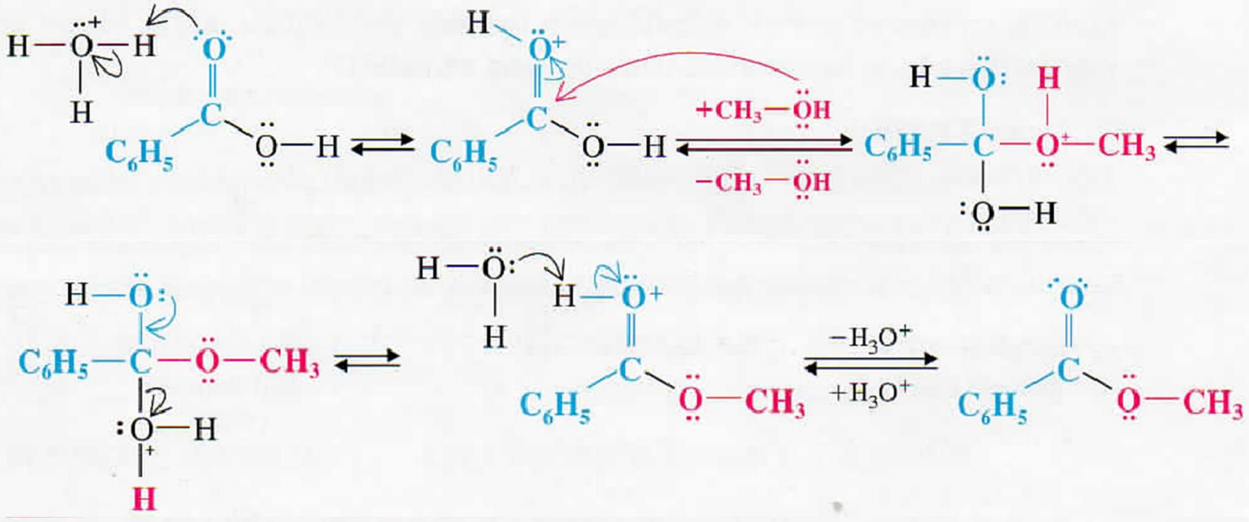
Fumaric acid

Problem 18.10 ➤ ^{18}O-Etiketli su içerisinde yapılan metil benzoatın asit katalizli hidrolizi sonunda etiketli oksijeni nerede bulmayı beklersiniz? Cevabınızı destekleyecek şekilde ayrıntılı bir mekanizma yazınız.

18.10 The labeled oxygen atom should appear in the carboxyl group of the acid. (Follow the reverse steps of the mechanism in Section 18.7A of the text using $H_2{}^{18}O$.)

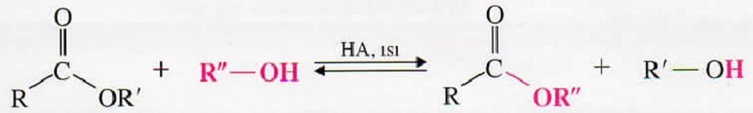


$$C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}-OH + CH_3-{}^{18}O-H \xrightleftharpoons{HA} C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}-{}^{18}OCH_3 + H_2O$$



◀ **Problem 18.11**

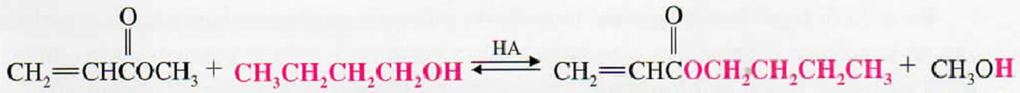
Esterler *transesterleşmeyle* de sentezlenebilirler:



$$R\overset{\overset{\displaystyle O}{\|}}{C}OR' + R''-OH \xrightleftharpoons{HA,\ ısı} R\overset{\overset{\displaystyle O}{\|}}{C}OR'' + R'-OH$$

Yüksek kaynama noktalı ester — **Yüksek kaynama noktalı alkol** — **Daha yüksek kaynama noktalı ester** — **Daha düşük kaynama noktalı alkol**

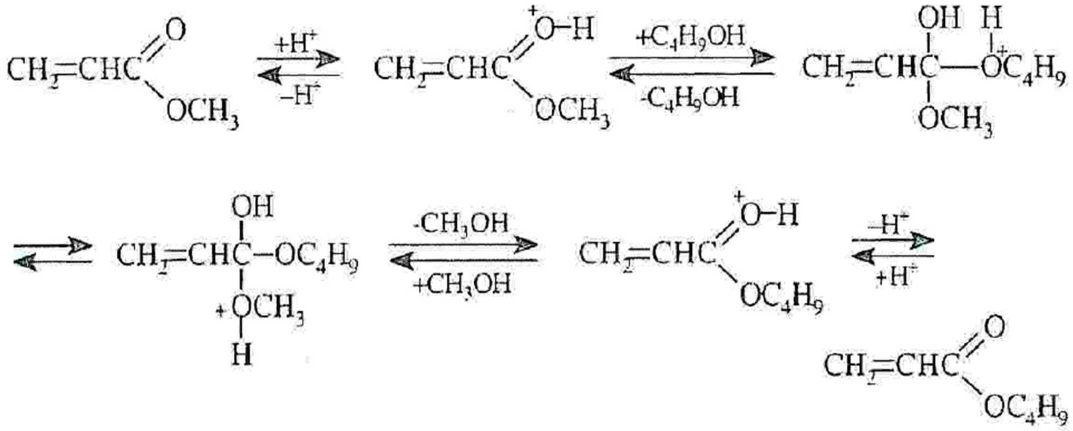
Bu yöntemde, dengenin yönü, düşük kaynama noktalı alkollerin tepkime karışımından damıtılarak uzaklaştırılmasıyla sağa kaydırılır. Transesterleşme tepkimesinin mekanizması asit-katalizli esterleşme (veya asit katalizli ester hidrolizi) tepkimesine benzer. Aşağıdaki transesterleşme için ayrıntılı bir mekanizma yazınız.



$$CH_2{=}CH\overset{\overset{\displaystyle O}{\|}}{C}OCH_3 + CH_3CH_2CH_2CH_2OH \xrightleftharpoons{HA} CH_2{=}CH\overset{\overset{\displaystyle O}{\|}}{C}OCH_2CH_2CH_2CH_3 + CH_3OH$$

Metil akrilat — **Bütil alkol** — **Bütil akrilat** (%94) — **Metanol**

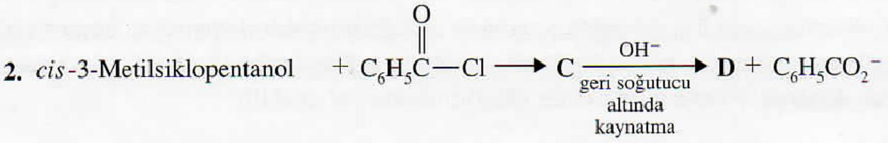
18.11



Problem 18.12

(a) A–F bileşiklerinin sterokimyasal formüllerini yazınız.

1. *cis*-3-Metilsiklopentanol + $C_6H_5SO_2Cl \longrightarrow \textbf{A} \xrightarrow[\text{ısı}]{OH^-} \textbf{B} + C_6H_5SO_3^-$



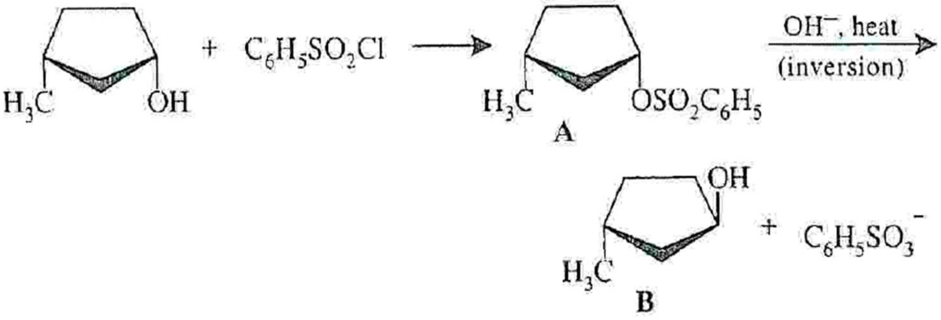
2. *cis*-3-Metilsiklopentanol $+ C_6H_5\overset{O}{\overset{\|}{C}}—Cl \longrightarrow \textbf{C} \xrightarrow[\text{geri soğutucu altında kaynatma}]{OH^-} \textbf{D} + C_6H_5CO_2^-$

3. (*R*)-2-Bromooktan + $CH_3CO_2^-Na^+ \longrightarrow \textbf{E} + NaBr \xrightarrow[\text{(geri soğutucu altında kaynatma)}]{OH^-,\ H_2O} \textbf{F}$

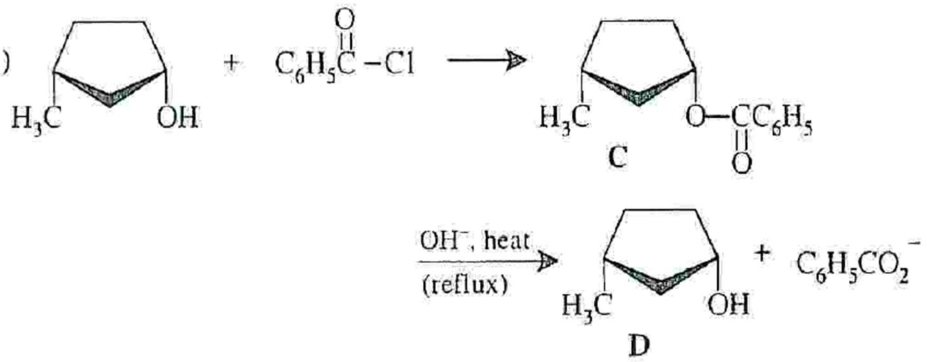
4. (*R*)-2-Bromooktan $+ OH^- \xrightarrow{\text{aseton}} \textbf{F} + Br^-$

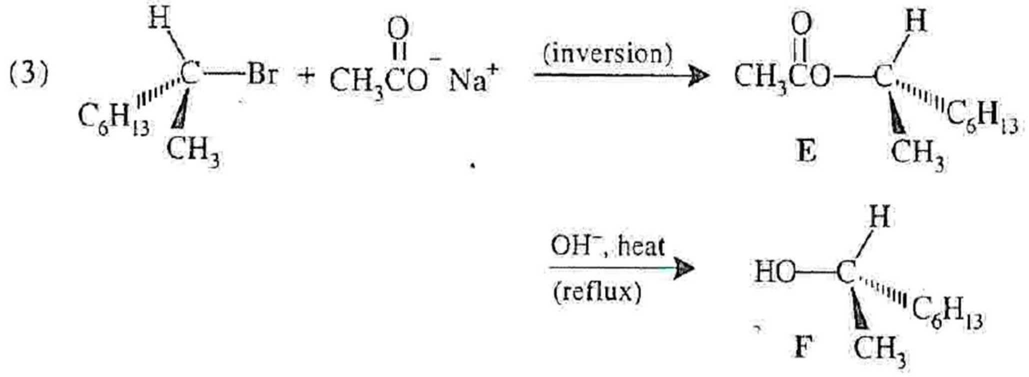
(b) Son iki yöntemde **(3)** veya **(4)**, hangisinde **F** daha yüksek verimle oluşur? Niçin?

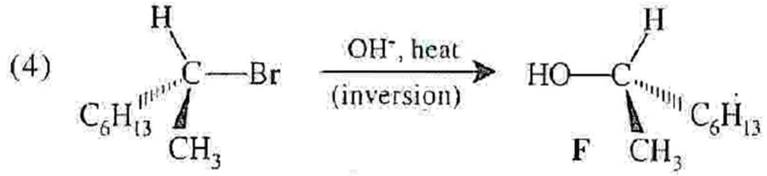
18.12 (a) (1)



(2)

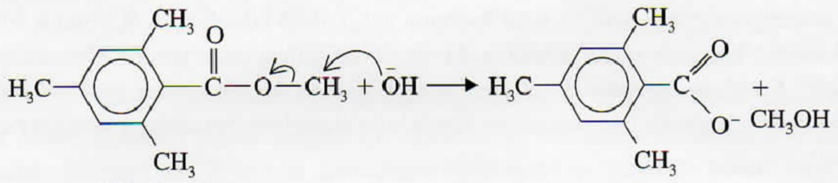






(b) Method (3) should give a higher yield of **F** than method (4). Since the hydroxide ion is a strong base and since the alkyl halide is secondary, method (4) is likely to be accompanied by considerable elimination. Method (3), on the other hand, employs a weaker base, acetate ion, in the S_N2 step and is less likely to be complicated by elimination. Hydrolysis of the ester **E** that results should also proceed in high yield.

Problem 18.13 ➤ Metil mesitoatın baz destekli hidrolizi açil karbonu yerine alkol karbonu üzerine atakla olur.



Metil mesitoat

(a) Bu beklenmeyen davranış için bir açıklama yapabilir misiniz?

(b) Bu tepkime için, atağın yukarıdaki gibi olduğunu gösteren, etiketli bir bileşiğin kullanıldığı bir deney öneriniz.

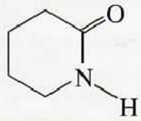
18.13 (a) Steric hindrance presented by the di-ortho methyl groups of methyl mesitoate prevents formation of the tetrahedral intermediate that must accompany attack at the acyl carbon.

(b) Carry out hydrolysis with labeled $^{18}OH^-$ in labeled $H_2{}^{18}O$. The label should appear in the methanol.

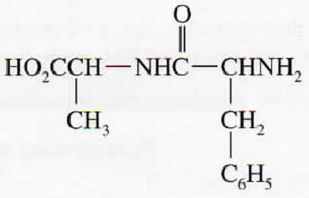
Aşağıdaki her bir amidin asidik ve bazik hidrolizleri sonucu hangi ürünleri elde edersiniz? ◄ **Problem 18.14**

(a) *N*,*N*-Dietilbenzamit

(b)



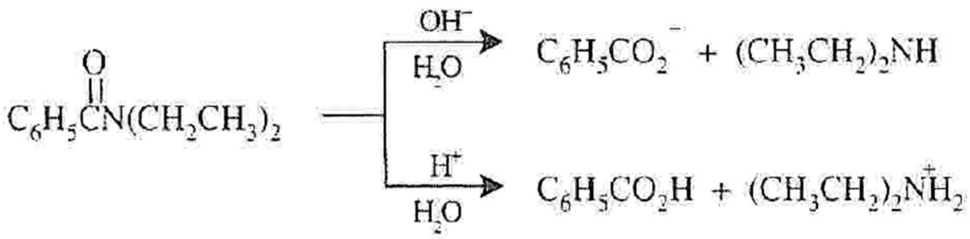
(c)



$\mathrm{HO_2C\underset{CH_3}{\underset{|}{C}H}{-}NH\overset{O}{\overset{\|}{C}}{-}\underset{C_6H_5}{\underset{|}{\underset{CH_2}{\underset{|}{C}H}}}NH_2}$

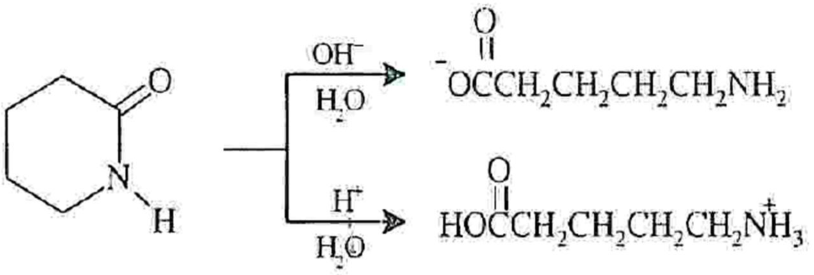
(bir dipeptit)

18.14 (a)



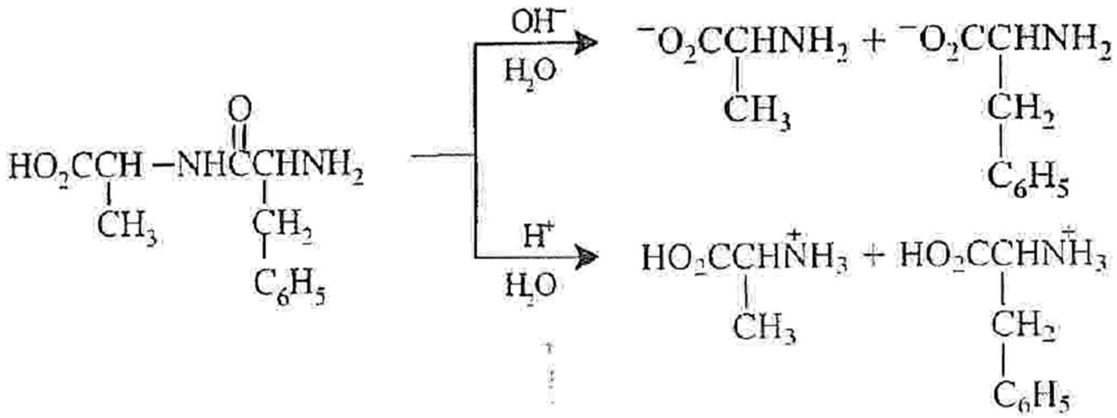
$$C_6H_5\overset{\overset{O}{\|}}{C}N(CH_2CH_3)_2 \begin{cases} \xrightarrow[H_2O]{OH^-} C_6H_5CO_2^- + (CH_3CH_2)_2NH \\ \xrightarrow[H_2O]{H^+} C_6H_5CO_2H + (CH_3CH_2)_2\overset{+}{N}H_2 \end{cases}$$

(b)



$$\begin{cases} \xrightarrow[H_2O]{OH^-} {}^-O\overset{\overset{O}{\|}}{C}CH_2CH_2CH_2CH_2NH_2 \\ \xrightarrow[H_2O]{H^+} HO\overset{\overset{O}{\|}}{C}CH_2CH_2CH_2CH_2\overset{+}{N}H_3 \end{cases}$$

(c)



$$HO_2C\underset{CH_3}{\underset{|}{C}}H-NH\overset{\overset{O}{\|}}{C}\underset{\underset{C_6H_5}{\underset{|}{CH_2}}}{\underset{|}{C}}HNH_2 \begin{cases} \xrightarrow[H_2O]{OH^-} {}^-O_2C\underset{CH_3}{\underset{|}{C}}HNH_2 + {}^-O_2C\underset{\underset{C_6H_5}{\underset{|}{CH_2}}}{\underset{|}{C}}HNH_2 \\ \xrightarrow[H_2O]{H^+} HO_2C\underset{CH_3}{\underset{|}{C}}H\overset{+}{N}H_3 + HO_2C\underset{\underset{C_6H_5}{\underset{|}{CH_2}}}{\underset{|}{C}}H\overset{+}{N}H_3 \end{cases}$$

Problem 18.15 ➤ **(a)** $(CH_3)_3CCO_2H$'den $(CH_3)_3CCN$ sentezinin bütün basamaklarını gösteriniz.

(b) Aşağıdaki yöntemle $(CH_3)_3CCN$ bileşiğini sentezlemek istediğinizde hangi ürünleri elde edersiniz?

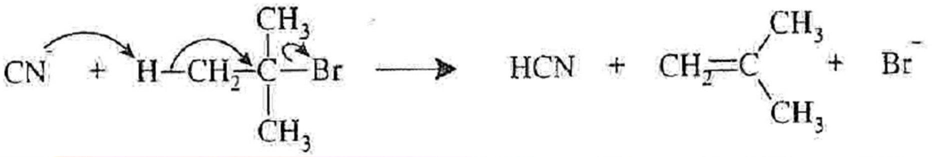
$$(CH_3)_3C—Br + CN^- \longrightarrow$$

18.15 (a)

$$(CH_3)_3CCO_2H \xrightarrow{SOCl_2} (CH_3)_3CCOCl \xrightarrow{NH_3} (CH_3)_3CCONH_2$$

$$\xrightarrow[heat]{P_4O_{10}} (CH_3)_3CC{\equiv}N$$

(b) An elimination reaction would take place because CN^- is a strong base.



$$CN^- + H-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br \longrightarrow HCN + CH_2{=}C(CH_3)_2 + Br^-$$

Problem 18.6 ➤ Aşağıdaki tepkimelerde oluşan ürünlerin yapılarını yazınız.

(a) $C_6H_5CH_2OH + C_6H_5N{=}C{=}O \longrightarrow$

(b) $ClCOCl$ + aşırı $CH_3NH_2 \longrightarrow$

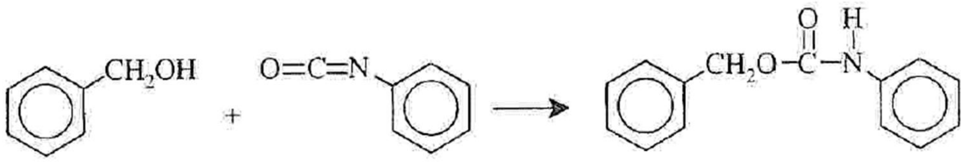
(c) Glisin ($H_3\overset{+}{N}CH_2CO_2^-$) + $C_6H_5CH_2OCOCl \xrightarrow{OH^-}$

(d) (c)'nin ürünü + H_2, Pd $\longrightarrow$

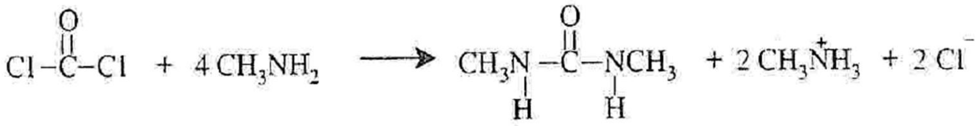
(e) (c)'nin ürünü + soğuk HBr, $CH_3CO_2H \longrightarrow$

(f) Üre + OH^-, H_2O, ısı $\longrightarrow$

18.16 (a)

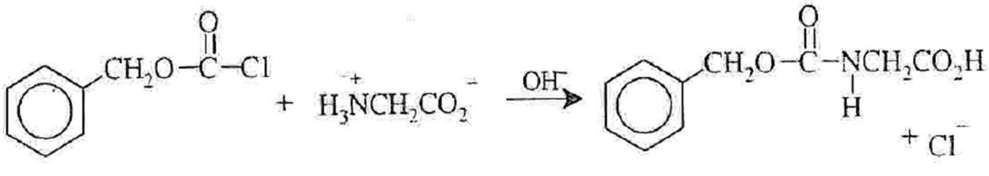


(b)

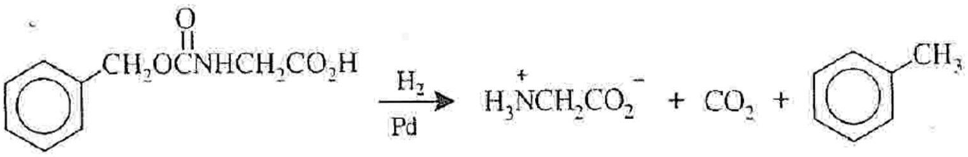


$$Cl-\overset{O}{\overset{\|}{C}}-Cl + 4\,CH_3NH_2 \longrightarrow CH_3\underset{H}{N}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}CH_3 + 2\,CH_3\overset{+}{N}H_3 + 2\,Cl^-$$

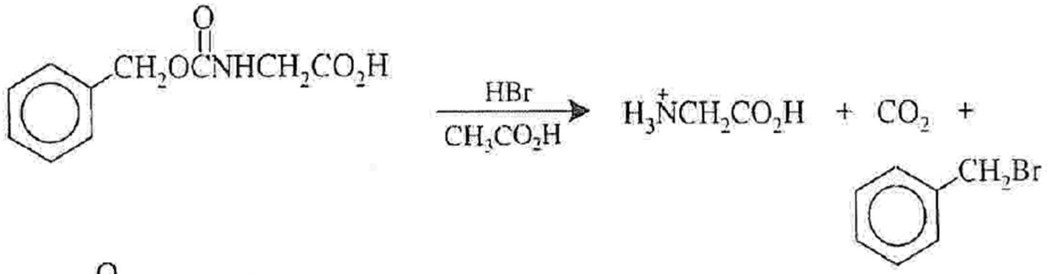
(c)



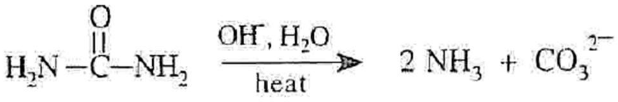
(d)



(e)



(f)



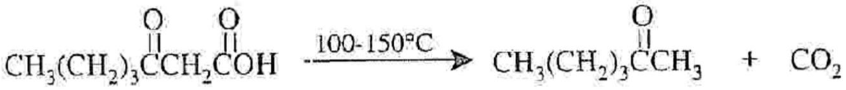
$$H_2N-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{heat}]{OH^-,\ H_2O} 2\,NH_3 + CO_3^{2-}$$

Problem 18.17

Dekarboksilasyon tepkimelerini kullanarak aşağıdaki maddelerin herbirini uygun başlangıç maddelerinden sentezleyiniz.

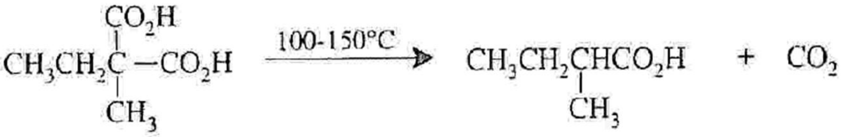
(a) 2-Heksanon
(b) 2-Metilbütanoik asit
(c) Sikloheksanon
(d) Pentanoik asit

18.17 (a) By decarboxylation of a β-keto acid:



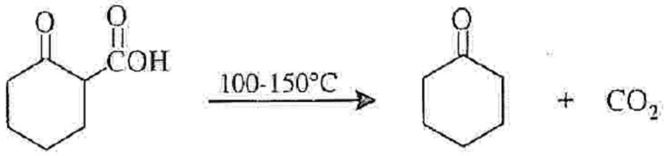
$$CH_3(CH_2)_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OH \xrightarrow{100\text{-}150°C} CH_3(CH_2)_3\overset{O}{\overset{\|}{C}}CH_3 + CO_2$$

(b) By decarboxylation of a substituted malonic acid:

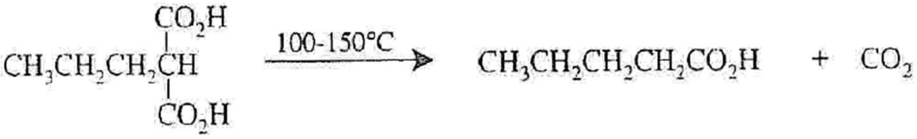


$$CH_3CH_2\underset{CH_3}{\overset{CO_2H}{C}}-CO_2H \xrightarrow{100\text{-}150°C} CH_3CH_2\underset{CH_3}{C}HCO_2H + CO_2$$

(c) By decarboxylation of a β-keto acid:

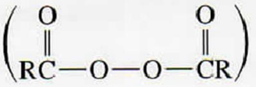


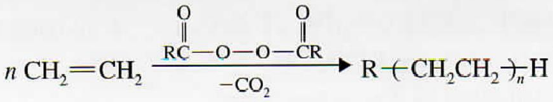
(d) By decarboxylation of a substituted malonic acid:



$$CH_3CH_2CH_2\underset{CO_2H}{\overset{CO_2H}{CH}} \xrightarrow{100\text{-}150°C} CH_3CH_2CH_2CH_2CO_2H + CO_2$$

Problem 18.18

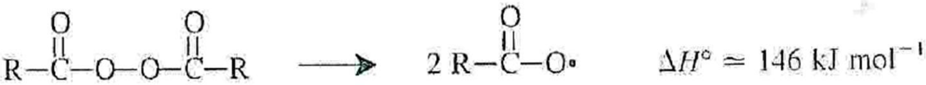
Diaçil peroksitler  $\left(R\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}R\right)$ ısıtıldıklarında hemen bozunurlar (a) Bu kararsızlığın nedeni nedir? (b) Diaçil peroksitin bozunmasıyla CO_2 oluşur. Bu dekarboksilasyon nasıl olmuştur? (c) Diaçil peroksitler radikal tepkimelerinde başlatıcı olarak kullanılırlar. Örneğin alkenlerin polimerleşmesinde:



$$n\,CH_2{=}CH_2 \xrightarrow[-CO_2]{R\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}R} R{+}CH_2CH_2{+}_nH$$

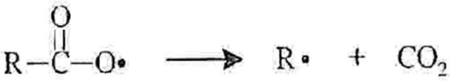
Tepkimenin basamaklarını gösteriniz.

18.18 (a) The oxygen-oxygen bond of the diacyl peroxide has a low homolytic bond dissociation energy ($DH° \simeq 146$ kJ mol^{-1}). This allows the following reaction to occur at a moderate temperature.



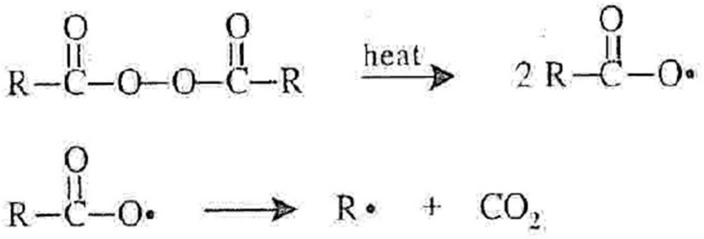
$$R-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-R \longrightarrow 2\,R-\overset{O}{\overset{\|}{C}}-O\cdot \qquad \Delta H° \simeq 146 \text{ kJ mol}^{-1}$$

(b) By decarboxylation of the carboxylate radical produced in part (a).



$$R-\overset{O}{\overset{\|}{C}}-O\cdot \longrightarrow R\cdot + CO_2$$

(c) ***Chain Initiation***



Step 1 $R-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-R \xrightarrow{\text{heat}} 2\,R-\overset{O}{\overset{\|}{C}}-O\cdot$

Step 2 $R-\overset{O}{\overset{\|}{C}}-O\cdot \longrightarrow R\cdot + CO_2$

Chain Propagation

Step 3 $R\cdot + CH_2=CH_2 \longrightarrow RCH_2CH_2\cdot$

Step 4 $RCH_2CH_2\cdot + CH_2=CH_2 \longrightarrow RCH_2CH_2CH_2CH_2\cdot$

Step 3, 4, 3, 4, and so on.

18.19 Aşağıdaki her bir bileşiğin yapı formülünü yazınız:

(a) Heksanoik asit
(b) Heksanamit
(c) *N*-Etilheksanamit
(d) *N,N*-Dietilheksanamit
(e) 3-Heksandiok asit
(f) 2-Metil-4-heksenoik asit
(g) Heksandiok asit
(h) Ftalik asit
(i) İzoftalik asit
(j) Tereftalik asit
(k) Dietil oksalat
(l) Dietil adipat
(m) İzobütil propanoat
(n) 2-Naftoik asit
(o) Maleik asit
(p) 2-Hidroksibütandiok asit (malik asit)
(q) Fumarik asit
(r) Süksinik asit asit
(s) Süksinimit
(t) Malonik asit
(u) Dietil malonat

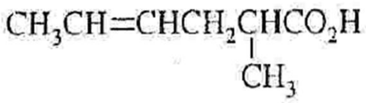
18.19 (a) $CH_3(CH_2)_4CO_2H$

(b) $CH_3(CH_2)_4CONH_2$

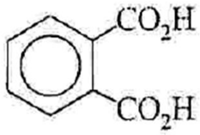
(c) $CH_3(CH_2)_4CONHC_2H_5$

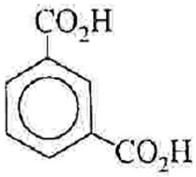
(d) $CH_3(CH_2)_4CON(C_2H_5)_2$

(e) $CH_3CH_2CH{=}CHCH_2CO_2H$

(f)

$CH_3CH{=}CHCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCO_2H$

(g) $HO_2CCH_2CH_2CH_2CH_2CO_2H$

(h)


(i)


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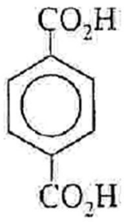
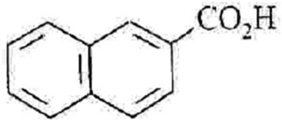
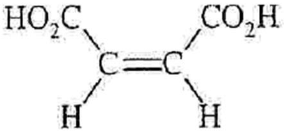


(k) $C_2H_5O_2C{-}CO_2C_2H_5$

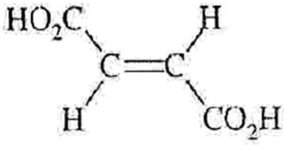
(l) $C_2H_5O_2C(CH_2)_4CO_2C_2H_5$

(m) $CH_3CH_2CO_2CH_2CH(CH_3)_2$

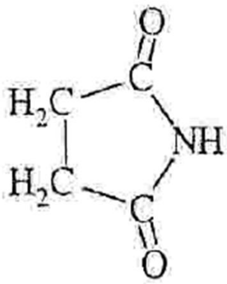
(n)


(o)


(p) $HO_2CCHOHCH_2CO_2H$

(q)


(r) $HO_2CCH_2CH_2CO_2H$

(s)


(t) $HO_2CCH_2CO_2H$

(u) $C_2H_5O_2CCH_2CO_2C_2H_5$

18.20 Aşağıdaki bileşiklerin her biri için IUPAC veya yaygın adını yazınız:

(a) $C_6H_5CO_2H$

(b) C_6H_5COC1

(c) $C_6H_5CONH_2$

(d) $(C_6H_5CO)_2O$

(e) $C_6H_5CO_2CH_2C_6H_5$

(f) $C_6H_5CO_2C_6H_5$

(g) $CH_3CO_2CH(CH_3)_2$

(h) $CH_3CON(CH_3)_2$

(i) CH_3CN

18.20 (a) Benzoic acid

(b) Benzoyl chloride

(c) Benzamide

(d) Benzoic anhydride

(e) Benzyl benzoate

(f) Phenyl benzoate

(g) Isopropyl acetate or 1-methylethyl ethanoate

(h) *N,N*-Dimethylacetamide or *N,N*-dimethylethanamide

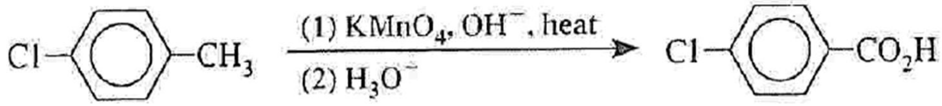
(i) Acetonitrile or ethanenitrile

18.21 *p*-Klorotoluenin aşağıdaki her bir bileşiğe nasıl dönüştürülebileceğini gösteriniz:

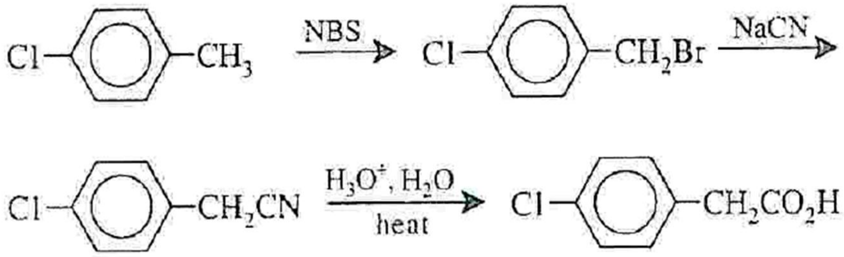
(a) *p*-Klorobenzoik asit **(c)** *p*-$ClC_6H_4CH(OH)CO_2H$

(b) *p*-Klorofenilasetik asit **(d)** *p*-$ClC_6H_4CH{=}CHCO_2H$

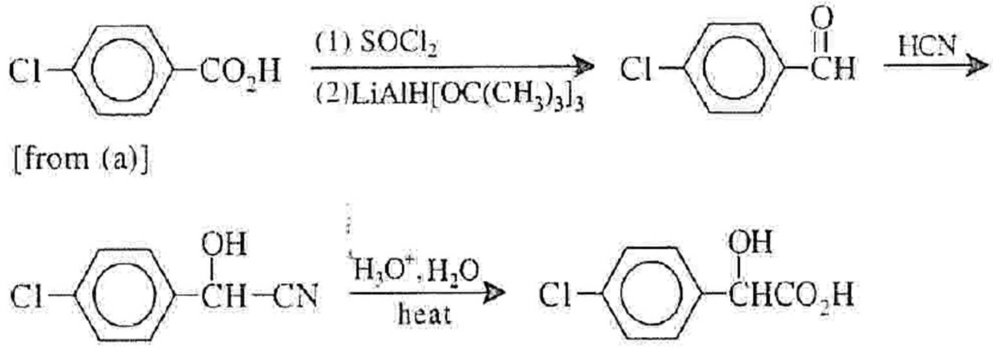
18.21 (a)



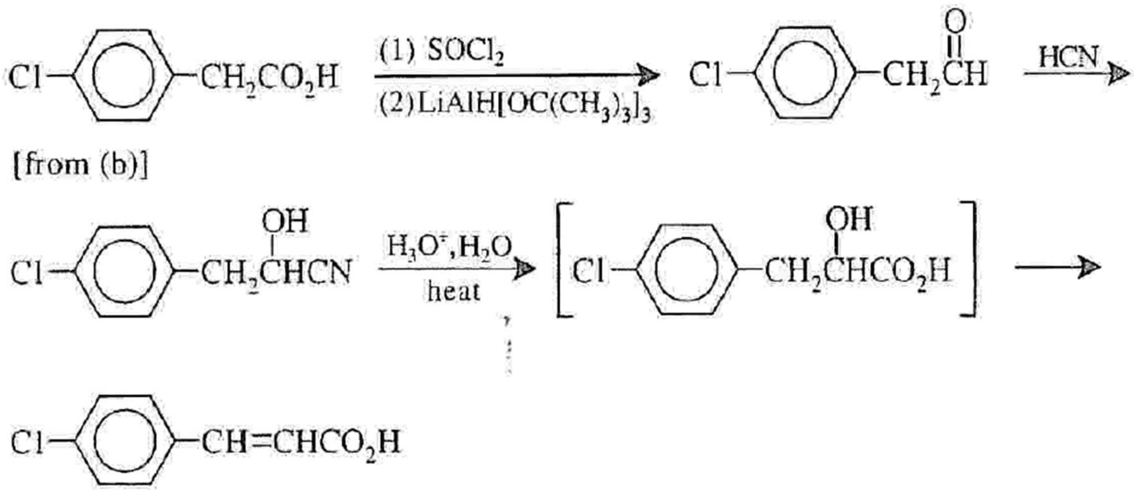
(b)



(c)



(d)



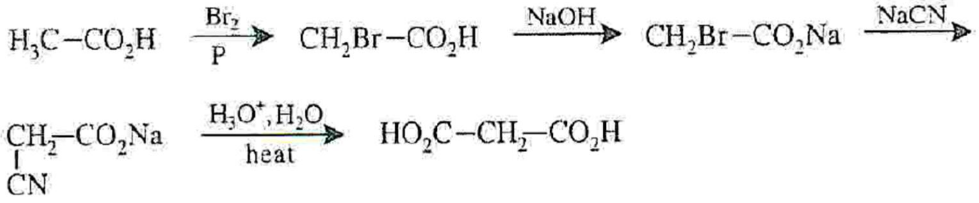
18.22 Aşağıdaki sentezleri yapınız.

(a) Asetik asitten malonik asit

(b) 1,4-Bütandiolden süksinik asit

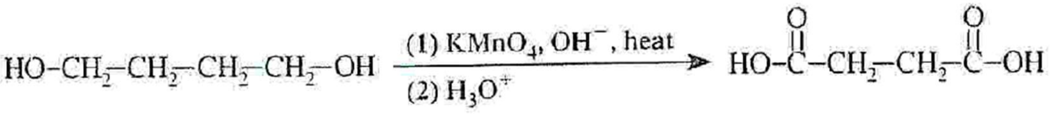
(c) Sikloheksanolden adipik asit

18.22 (a)



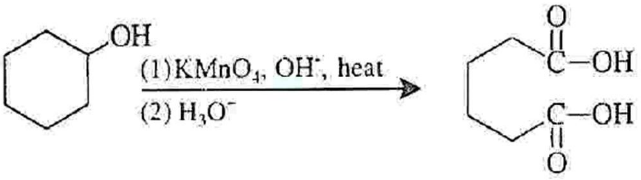
$$H_3C-CO_2H \xrightarrow[P]{Br_2} CH_2Br-CO_2H \xrightarrow{NaOH} CH_2Br-CO_2Na \xrightarrow{NaCN} \underset{\displaystyle CN}{CH_2}-CO_2Na \xrightarrow[heat]{H_3O^+,\,H_2O} HO_2C-CH_2-CO_2H$$

(b)



$$HO-CH_2-CH_2-CH_2-CH_2-OH \xrightarrow[(2)\ H_3O^+]{(1)\ KMnO_4,\ OH^-,\ heat} HO-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

(c)



18.23 Aşağıdaki bileşiklerin her birinden pentanoik asitin nasıl sentezlenebileceğini gösteriniz.

(a) 1-Pentanol	**(c)** 5-Deken
(b) 1-Bromobütan (iki yol)	**(d)** Pentanal

18.23 (a) $CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[(2)\ H_3O^+]{(1)\ KMnO_4,\ OH^-,\ heat} CH_3CH_2CH_2CH_2CO_2H$

(b) $CH_3CH_2CH_2CH_2Br \xrightarrow[(2)\ CO_2]{(1)\ Mg,\ Et_2O} CH_3CH_2CH_2CH_2CO_2MgBr \xrightarrow{H_3O^+} CH_3CH_2CH_2CH_2CO_2H$

$CH_3CH_2CH_2CH_2Br \xrightarrow{CN^-} CH_3CH_2CH_2CH_2CN \xrightarrow[heat]{H_3O^+,\ H_2O} CH_3CH_2CH_2CH_2CO_2H$

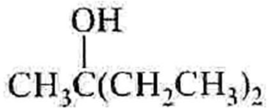
(c) $CH_3(CH_2)_3CH{=}CH(CH_2)_3CH_3 \xrightarrow[(2)\ H_3O^+]{(1)\ KMnO_4,\ OH^-,\ heat} 2\ CH_3(CH_2)_3CO_2H$

(d) $CH_3CH_2CH_2CH_2CHO \xrightarrow[(2)\ H_3O^-]{(1)\ Ag(NH_3)_2^+OH^-} CH_3CH_2CH_2CH_2CO_2H$

18.24 Asetil klorürün aşağıdaki maddelerin her biri ile olan tepkimesinde oluşan ana organik ürün nedir?

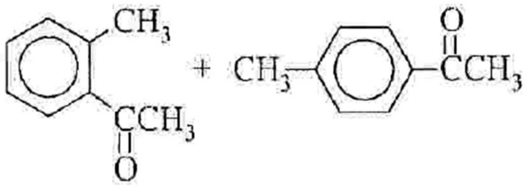
(a) H_2O
(b) CH_3CH_2Li (aşırı)
(c) $CH_3(CH_2)_2CH_2OH$ ve piridin
(d) NH_3 (aşırı)
(e) $C_6H_5CH_3$ ve $AlCl_3$
(f) $LiAlH[OC(CH_3)_3]_3$
(g) $(CH_3)_2CuLi$
(h) $NaOH/H_2O$
(i) CH_3NH_2 (aşırı)
(j) $C_6H_5NH_2$ (aşırı)
(k) $(CH_3)_2NH$ (aşırı)
(l) CH_3CH_2OH ve piridin
(m) $CH_3CO_2^-Na^+$
(n) CH_3CO_2H ve piridin
(o) Fenol ve piridin
(p) NBS, HBr, ve $SOCl_2$

18.24 (a) $CH_3CO_2H + HCl$

(b) 
$CH_3\overset{OH}{\overset{|}{C}}(CH_2CH_3)_2$

(c) $CH_3CO_2CH_2(CH_2)_2CH_3$

(d) CH_3CONH_2

(e) 

(f) CH_3CHO

(g) CH_3COCH_3

(h) CH_3CO_2Na

(i) $CH_3CONHCH_3$

(j) $CH_3CONHC_6H_5$

(k) $CH_3CON(CH_3)_2$

(l) $CH_3CO_2CH_2CH_3$

(m) $(CH_3CO)_2O$

(n) $(CH_3CO)_2O$

(o) $CH_3CO_2C_6H_5$

(p) $BrCH_2COCl$

18.25 Asetik anhidritin aşağıdaki maddelerin her biriyle olan tepkimesinde oluşan ana organik ürün nedir?

(a) NH_3 (fazla)	**(c)** $CH_3CH_2CH_2OH$	**(e)** $CH_3CH_2NH_2$ (aşırı)
(b) H_2O	**(d)** $C_6H_6 + A1C1_3$	**(f)** $(CH_3CH_2)_2NH$ (aşırı)

18.25 (a) $CH_3CONH_2 \ + \ CH_3CO_2^- \ NH_4^+$

(b) $2\,CH_3CO_2H$

(c) $CH_3CO_2CH_2CH_2CH_3 \ + CH_3CO_2H$

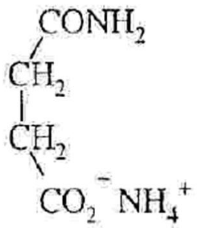
(d) $C_6H_5COCH_3 \ + CH_3CO_2H$

(e) $CH_3CONHCH_2CH_3 \ + CH_3CO_2^- \ CH_3CH_2NH_3^+$

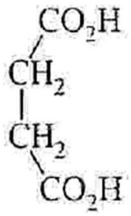
(f) $CH_3CON(CH_2CH_3)_2 \ + \ CH_3CO_2^- \ (CH_3CH_2)_2NH_2^+$

18.26 Problem 18.25'teki her bir reaktif süksinik anhidritle tepkimeye girdiğinde oluşan ana organik ürün nedir?

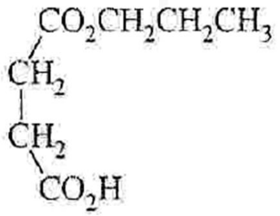
18.26 (a)



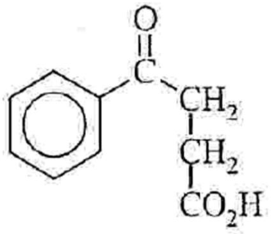
(b)



(c)



(d)



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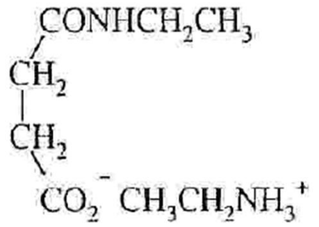
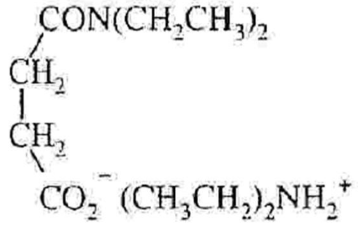


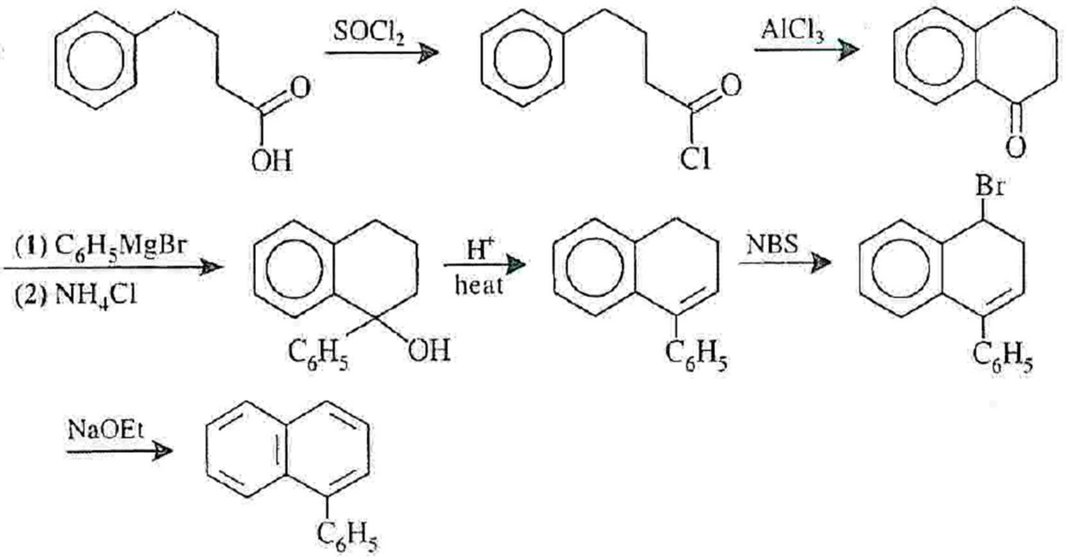
(f)



18.27 1-Fenilnaftalinin sentezini, benzen ve süksinik anhidritten başlayarak ve gerekli başka reaktifleri kullanarak gösteriniz.

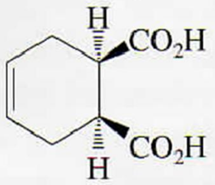
See text, p. 677.

18.27

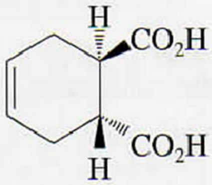


18.28 Aşağıdaki her bir bileşiği *cis*- veya *trans*- $HO_2C—CH=CH—CO_2H$'den (yani, maleik asit veya fumarik asitten) başlayarak ve gerekli başka maddeleri kullanarak sentezleyiniz.

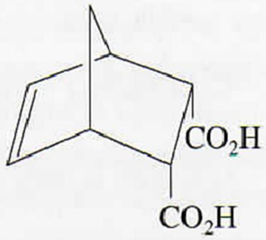
(a)



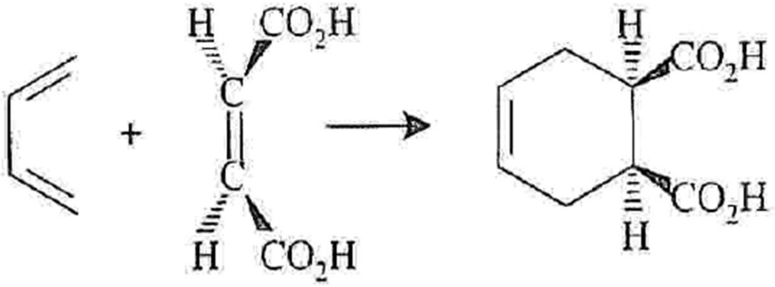
(b)



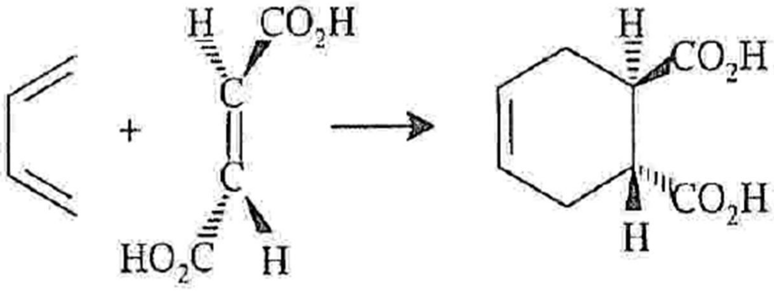
(c)



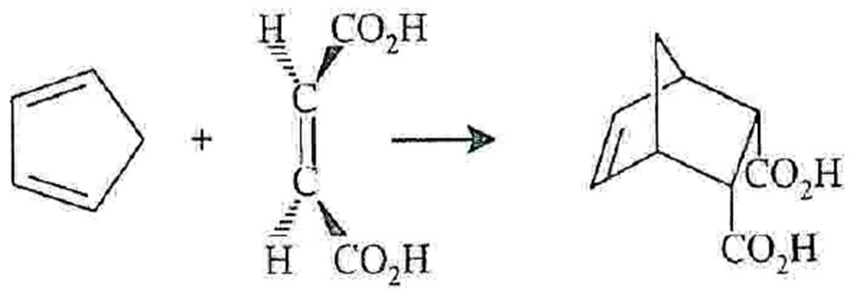
18.28 (a)



(b)



(c)



18.29 Aşağıdakilerin her biriyle etil propanoatın tepkimesinden hangi ürünler elde edilir?

(a) H_3O^+, H_2O **(c)** 1-Oktanol, HC1 **(e)** $LiA1H_4$, sonra H_2O

(b) OH^-, H_2O **(d)** CH_3NH_2 **(f)** Aşırı C_6H_5MgBr, sonra H_2O

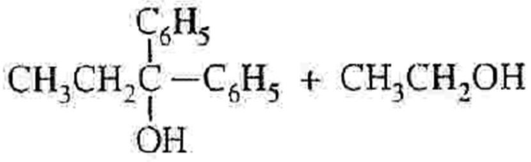
18.29 (a) $CH_3CH_2CO_2H + CH_3CH_2OH$

(b) $CH_3CH_2CO_2^- + CH_3CH_2OH$

(c) $CH_3CH_2CO_2(CH_2)_7CH_3 + CH_3CH_2OH$

(d) $CH_3CH_2CONHCH_3 + CH_3CH_2OH$

(e) $CH_3CH_2CH_2OH + CH_3CH_2OH$

(f) 

$CH_3CH_2C(C_6H_5)(OH)-C_6H_5 + CH_3CH_2OH$

18.30 Aşağıdakilerin her biriyle propanamit tepkimeye girdiğinde hangi ürünler elde edilir?

(a) H_3O^+, H_2O **(b)** OH^-, H_2O **(c)** P_4O_{10} ve ısı

18.30 (a) $CH_3CH_2CO_2H + NH_4^+$

(b) $CH_3CH_2CO_2^- + NH_3$

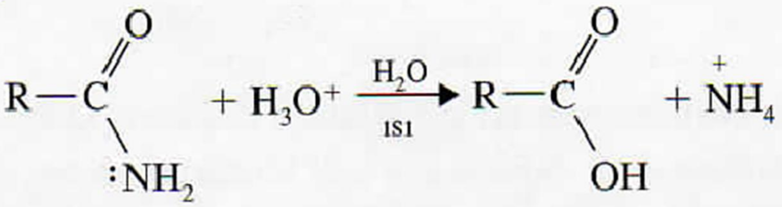
(c) CH_3CH_2CN

18.31 Problem 18.30 (a) ve (b) için ayrıntılı mekanizmaları yazınız.

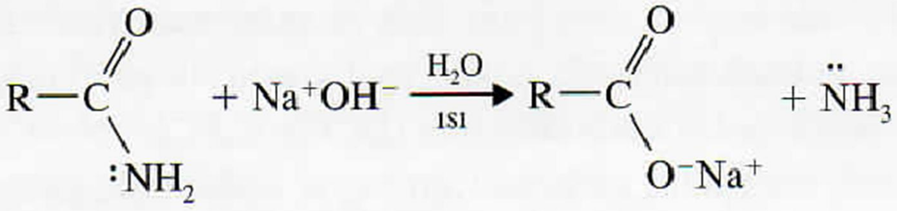
18.31 See the mechanisms in Section 18.8F, where R = CH_2CH_3 for propanamide.

Amitler sulu asit veya sulu baz içerisinde ısıtıldığında hidroliz olurlar.

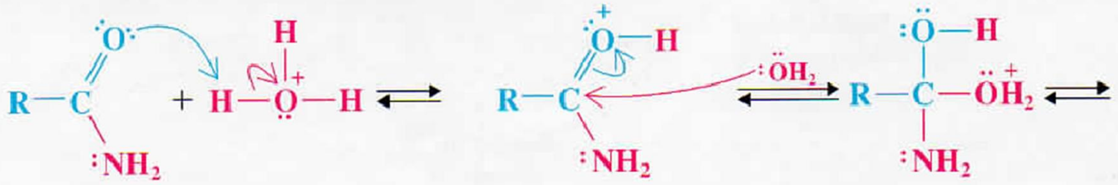
Asidik Hidroliz



Bazik Hidroliz



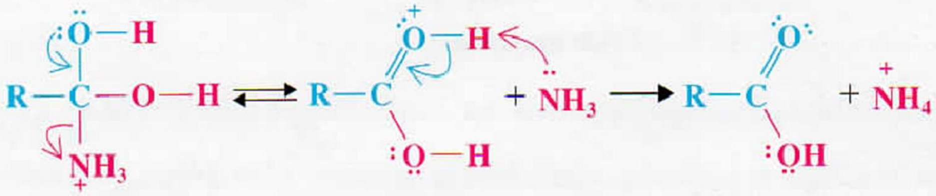
Bir Amidin Asidik Hidrolizi



Amit sulu asitten bir proton alır.

Bir su molekülü, protonlanmış karbonile atak yaparak bir düzgün dörtyüzlü ara ürün oluşturur.

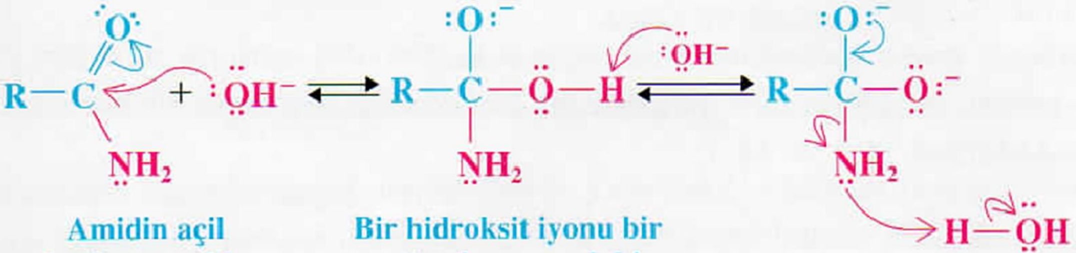
Oksijen üzerindeki proton çıkar ve azota bağlanır.



Amonyak molekülünün ayrılmasıyla protonlanmış karboksilik asit oluşur.

Amonyağa bir proton aktarılması sonucu karboksilik asit ve amonyum iyonu oluşur.

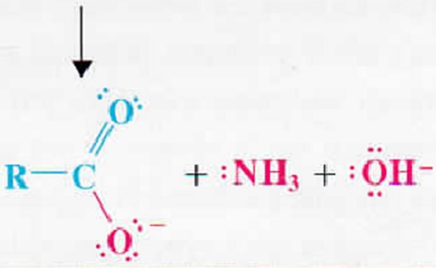
Bir Amidin Bazik Hidrolizi



Amidin açil karbonuna bir hidroksit iyonu atak yapar.

Bir hidroksit iyonu bir proton kopararak bir dianyon oluşturur.

Dianyon, bir amonyak (veya bir amin) molekülü kaybeder; bu basamak, sudan bir proton aktarılması ile eş zamanlıdır.



18.32 Aşağıdaki bileşiklerin her birinin ısıtılmasıyla hangi ürünler elde edilir.

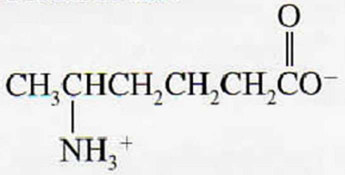
(a) 4-Hidroksibütanoik asit

(b) 3-Hidroksibütanoik asit

(c) 2-Hidroksibütanoik asit

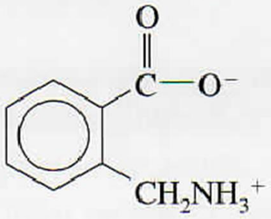
(d) Glutarik asit

(e)

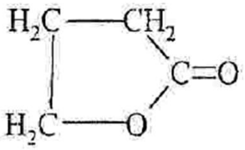


$CH_3CH(NH_3^+)CH_2CH_2CH_2CO_2^-$

(f)

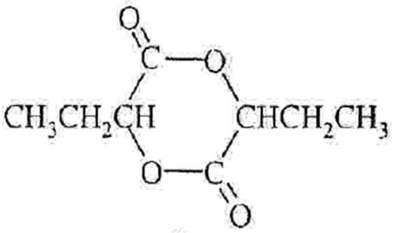


18.32 (a)

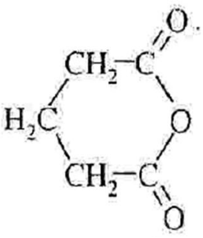


(b) $CH_3CH{=}CHCO_2H$

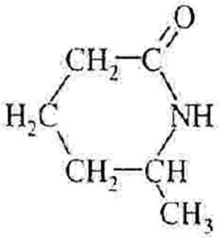
(c)



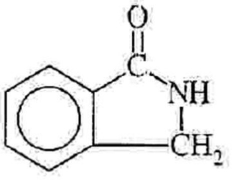
(d)



(e)



(f)



18.33 **A–Q** bileşiklerinin stereokimyasal formüllerini yazınız.

(a) $(R)\text{-}(-)\text{-2-Bütanol} \xrightarrow[\text{piridin}]{p\text{-toluensülfonil klorür (TsCl)}} \mathbf{A} \xrightarrow{CN^-} \mathbf{B}\ (C_5H_9N) \xrightarrow[H_2O]{H_2SO_4}$

$(+)\text{-}\mathbf{C}\ (C_5H_{10}O_2) \xrightarrow[(2)\ H_2O]{(1)\ LiAlH_4} (-)\text{-}\mathbf{D}\ (C_5H_{12}O)$

(b) $(R)\text{-}(-)\text{-2-Bütanol} \xrightarrow[\text{piridin}]{PBr_3} \mathbf{E}\ (C_4H_9Br) \xrightarrow{CN^-} \mathbf{F}\ (C_5H_9N) \xrightarrow[H_2O]{H_2SO_4}$

$(-)\text{-}\mathbf{C}\ (C_5H_{10}O_2) \xrightarrow[(2)\ H_2O]{(1)\ LiAlH_4} (+)\text{-}\mathbf{D}\ (C_5H_{12}O)$

(c) $\mathbf{A} \xrightarrow{CH_3CO_2^-} \mathbf{G}(C_6H_{12}O_2) \xrightarrow{OH^-} (+)\text{-}\mathbf{H}\ (C_4H_{10}O) + CH_3CO_2^-$

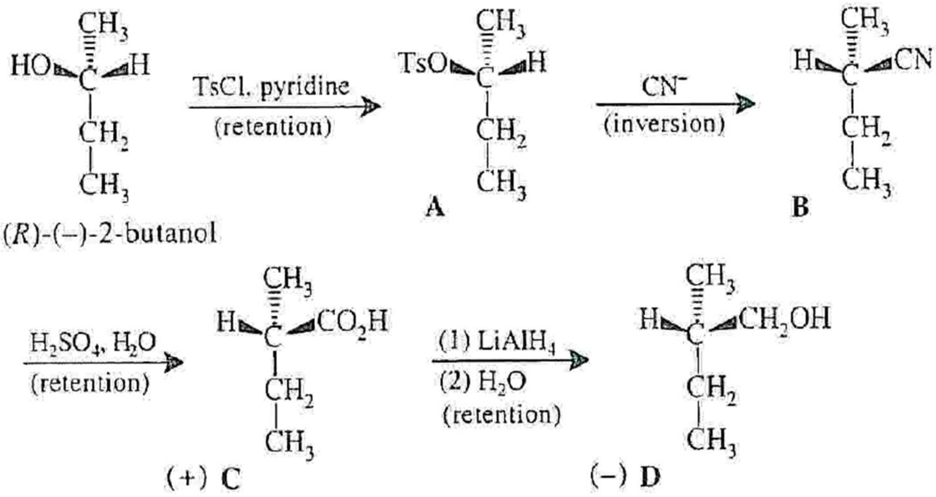
(d) $(-)\text{-}\mathbf{D} \xrightarrow{PBr_3} \mathbf{J}\ (C_5H_{11}Br) \xrightarrow[Et_2O]{Mg} \mathbf{K}\ (C_5H_{11}MgBr) \xrightarrow[(2)\ H_3O^+]{(1)\ CO_2} \mathbf{L}\ (C_6H_{12}O_2)$

(e) $(R)\text{-}(+)\text{-Gliseraldehit} \xrightarrow{HCN} \underbrace{\mathbf{M}\ (C_4H_7NO_3) + \mathbf{N}\ (C_4H_7NO_3)}_{\textbf{Diastereomerler, ayrımsal kristallendirmeyle ayrılır.}}$

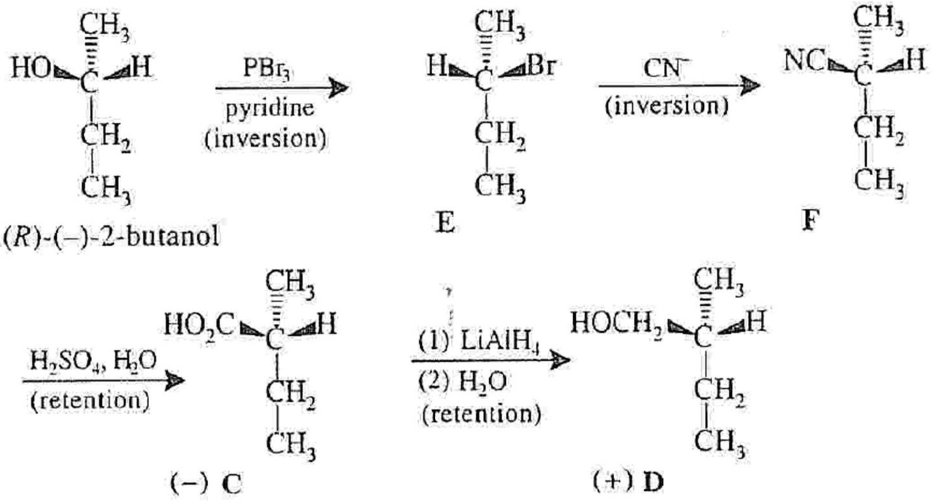
(f) **M** $\xrightarrow[H_2O]{H_2SO_4}$ **P** ($C_4H_8O_5$) $\xrightarrow[HNO_3]{[O]}$ *mezo*-tartarik asit

(g) **N** $\xrightarrow[H_2O]{H_2SO_4}$ **Q**($C_4H_8O_5$) $\xrightarrow[HNO_3]{[O]}$ (−)-tartarik asit

18.33 (a)



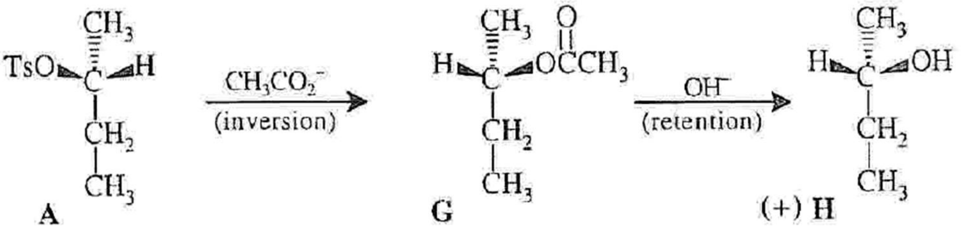
(b)



(*R*)-(−)-2-butanol **E** **F**

(−) **C** (+) **D**

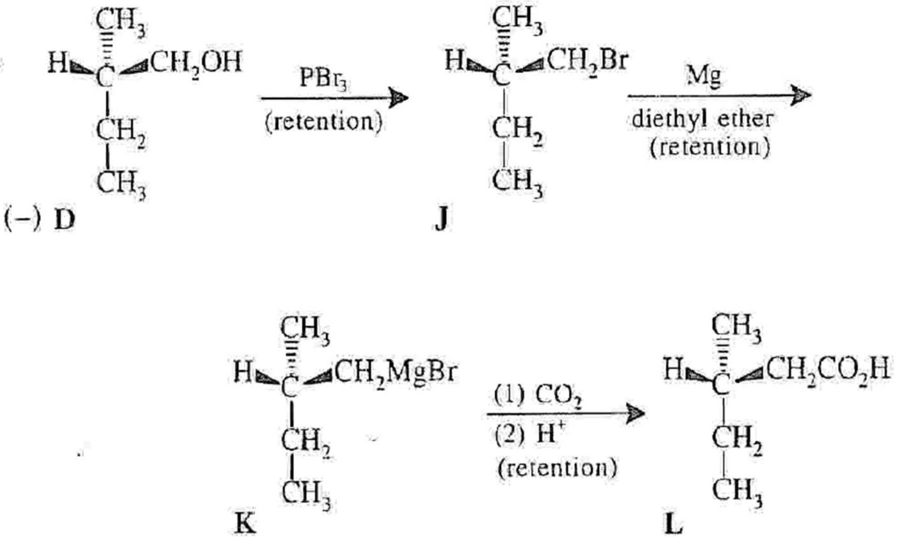
(c)



A **G** (+) **H**

(*S*)-(+)-2-butanol

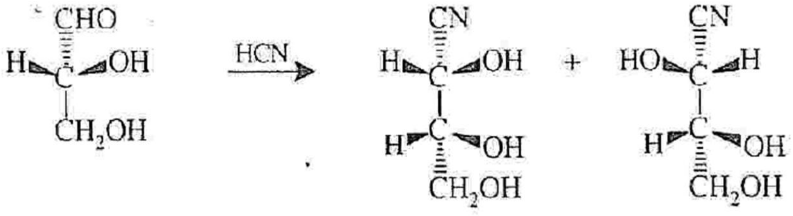
(d)



(−) **D** **J**

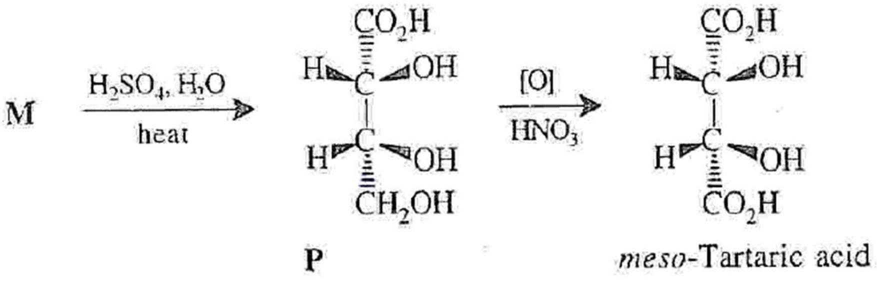
K **L**

(e)

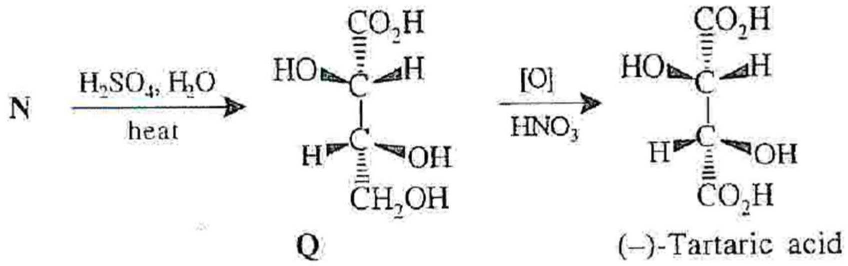


(*R*)-(+)-Glyceraldehyde **M** **N**

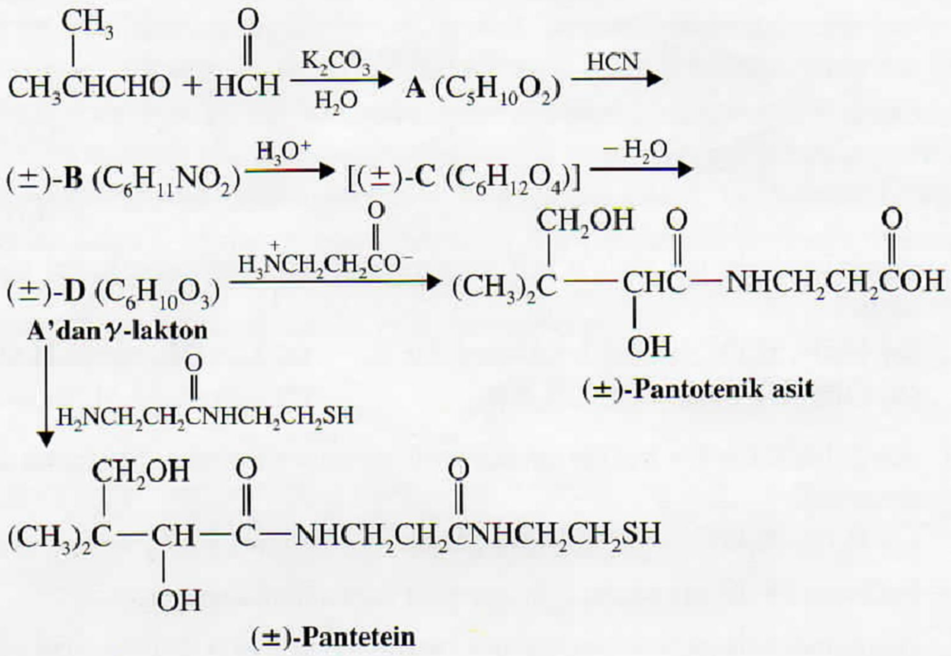
(f)



(g)

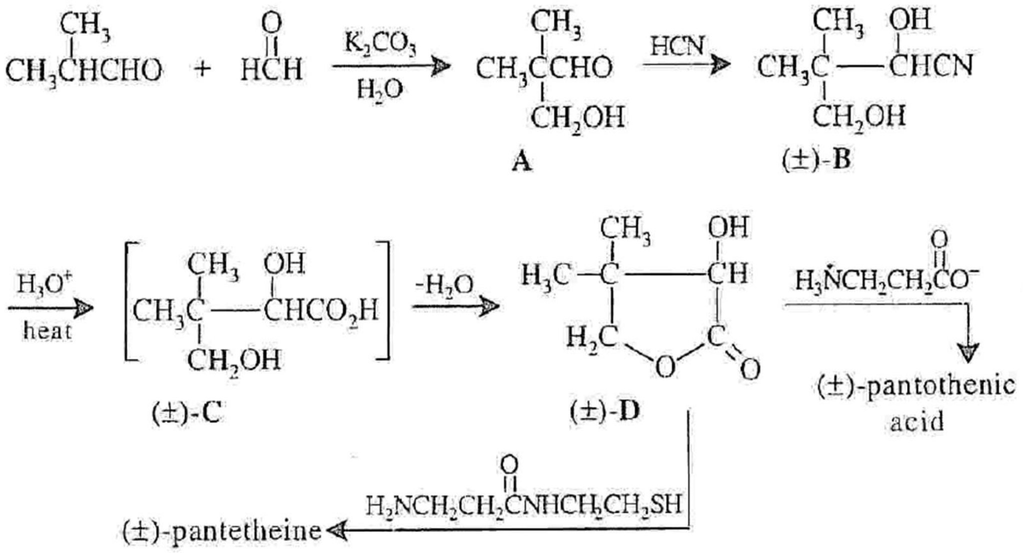


18.34 **(a)** (±)-Pantetein ve (±)-pantotenik asit, koenzim A'nın sentezinde önemli ara ürünlerdir ve aşağıdaki yöntemle hazırlanmışlardır. **A – D** bileşiklerinin yapılarını yazınız.

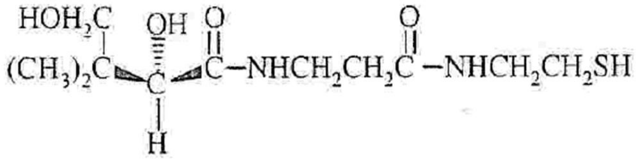

$CH_3CH(CH_3)CHO + HCHO$
K_2CO_3
H_2O
A ($C_5H_{10}O_2$)
HCN
(±)-**B** ($C_6H_{11}NO_2$)
H_3O^+
[(±)-**C** ($C_6H_{12}O_4$)]
$-H_2O$
(±)-**D** ($C_6H_{10}O_3$)
A'dan γ-lakton
$H_3\overset{+}{N}CH_2CH_2CO^-$
$(CH_3)_2C(CH_2OH)—CH(OH)C(=O)—NHCH_2CH_2COOH$
(±)-Pantotenik asit
$H_2NCH_2CH_2C(=O)NHCH_2CH_2SH$
$(CH_3)_2C(CH_2OH)—CH(OH)—C(=O)—NHCH_2CH_2C(=O)NHCH_2CH_2SH$
(±)-Pantetein

(b) γ-Lakton, (±)-**D,** yarılabilir. Pantetein sentezinin son basamağında (–)-γ-lakton kullanıldığında, doğal olarak oluşan pantetein ile aynı yapı elde edilir. (–)-γ-lakton (*R*) konfigürasyonuna sahiptir. Doğal olarak oluşan panteteinin stereokimyası nedir? **(c)** (±)-Pantetein sulu sodyum hidroksit içerisinde ısıtıldığında oluşan ürünler nelerdir.

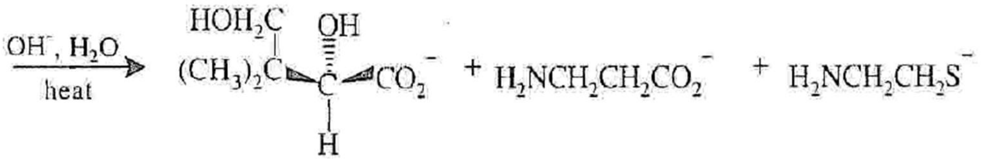
18.34 (a)



(b)

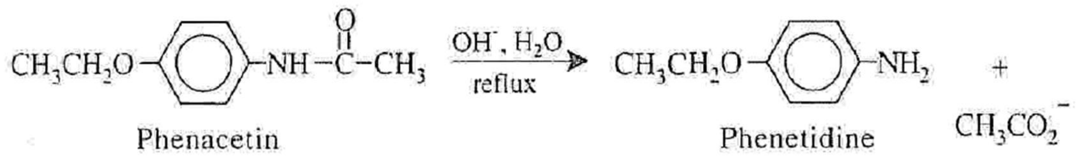


(c)



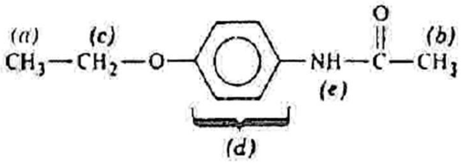
18.35 Fenasetinin ($C_{10}H_{13}NO_2$) IR ve ^{1}H NMR spektrumları Şekil 18.5'te verilmiştir. Fenasetin ağrı kesici ve ateş düşürücü bir maddedir ve A-P-C tabletlerinin (**a**spirin-**p**henasetin-**c**affein) P'sidir. (Fenasetin, toksik özelliğinden dolayı tıbbi olarak artık kullanılmamaktadır.) Fenasetin sulu sodyum hidroksit ile ısıtıldığında fenetidin ($C_8H_{11}NO$) ve sodyum asetat oluşur. Fenasetin ve fenetidinin yapılarını tahmin ediniz.

18.35



$CH_3CH_2O-C_6H_4-NH-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\text{reflux}]{OH^-,\ H_2O} CH_3CH_2O-C_6H_4-NH_2 + CH_3CO_2^-$

An interpretation of the ^{1}H NMR spectral data for phenacetin is as follows:



(*a*) triplet δ 1.4

(*b*) singlet δ 2.1

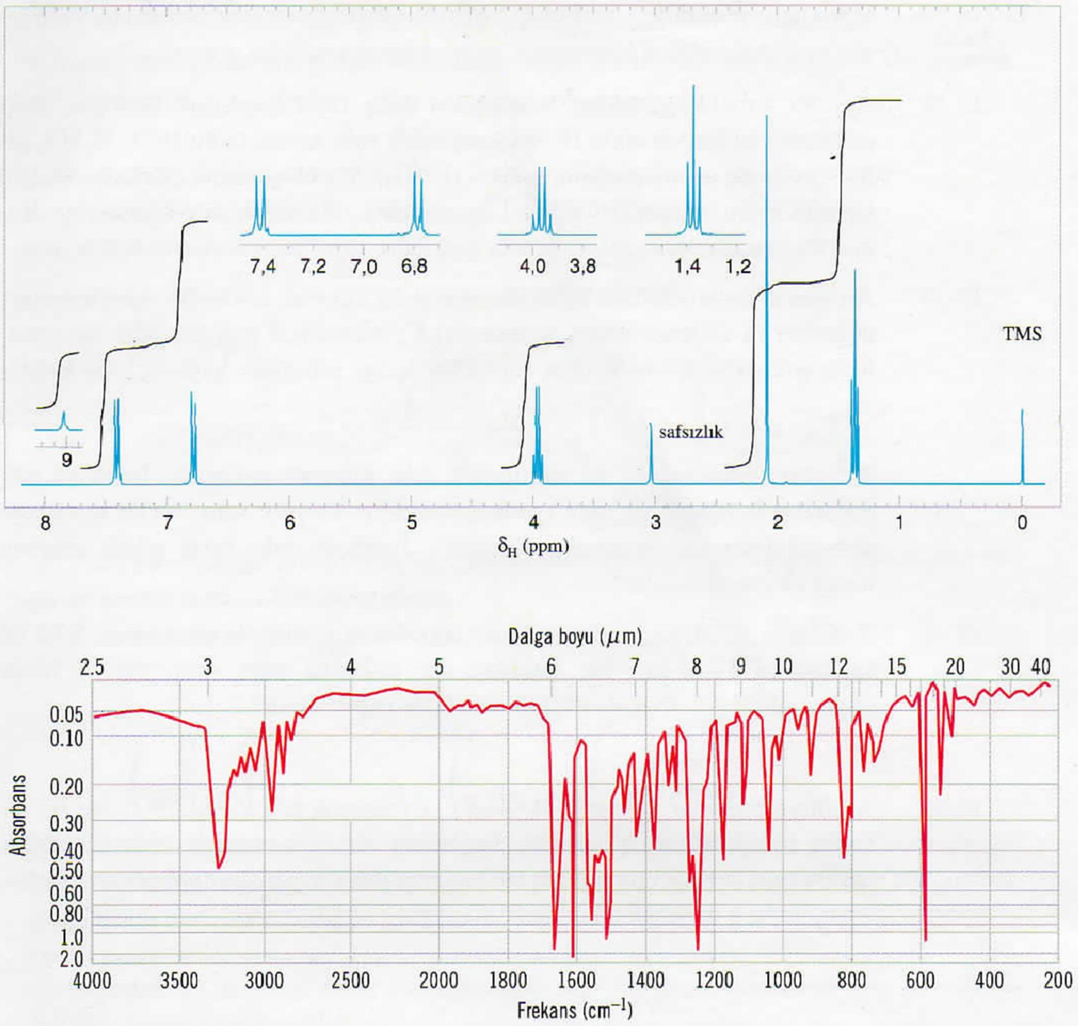
(*c*) quartet δ 3.95

(*d*) multiplet δ 6.8-7.4

(*e*) broad singlet δ 9.0

18.36 Aşağıda ^{1}H NMR spektrumu ve karbonil İR soğurma pikleri verilen beş açil bileşiğinin her birine bir yapı öneriniz.

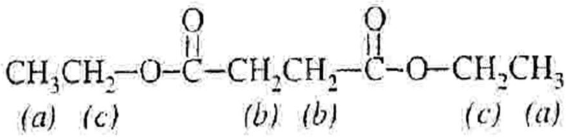
(a) $C_8H_{14}O_4$	^{1}H NMR spektrumu		İR spektrumu
	Üçlü	δ 1,2 (6H)	1740 cm^{-1}
	Birli	δ 2,5 (4H)	
(b) $C_{11}H_{14}O_2$	Dörtlü	δ 4,1 (4H)	
	^{1}H NMR spektrumu		İR spektrumu
	İkili	δ 1,0 (6H)	1720 cm^{-1}
	Çoklu	δ 2,1 (1H)	
	İkili	δ 4,1 (2H)	
	Çoklu	δ 7,8 (5H)	



Şekil 18.5 Fenasetinin 300 MHz ^{1}H NMR ve İR spektrumları. ^{1}H NMR piklerinin genişletilmiş şekilleri kaydırılmış olarak ayrıca gösterilmiştir. (İnfrared spektrumu Sadtler Araştırma Laboratuvarından alınmıştır, Philadelphia.)

(c) $C_{10}H_{12}O_2$	^{1}H NMR spektrumu		İR spektrumu
	Üçlü	δ 1,2 (3H)	1740 cm^{-1}
	Birli	δ 3,5 (2H)	
	Dörtlü	δ 4,1 (2H)	
	Çoklu	δ 7,3 (5H)	
(d) $C_2H_2Cl_2O_2$	^{1}H NMR spektrumu		İR spektrumu
	Birli	δ 6,0	2500–2700 cm^{-1} geniş pik
	Birli	δ 11,70	1705 cm^{-1}
(e) $C_4H_7ClO_2$	^{1}H NMR spektrumu		İR spektrumu
	Üçlü	δ 1,3	1745 cm^{-1}
	Birli	δ 4,0	
	Dörtlü	δ 4,2	

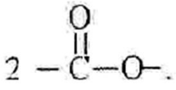
18.36 (a)



$$\underset{(a)}{CH_3}\underset{(c)}{CH_2}-O-\overset{O}{\overset{\|}{C}}-\underset{(b)}{CH_2}\underset{(b)}{CH_2}-\overset{O}{\overset{\|}{C}}-O-\underset{(c)}{CH_2}\underset{(a)}{CH_3}$$

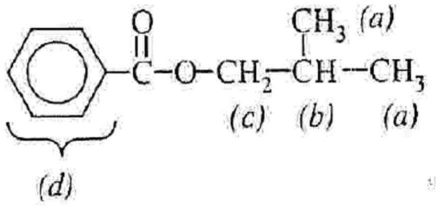
Interpretation:

(a) Triplet δ 1.2 (6H)
(b) Singlet δ 2.5 (4H)
(c) Quartet δ 4.1 (4H)



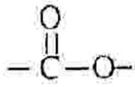
2 $-\overset{O}{\overset{\|}{C}}-O-$, 1740 cm^{-1} (ester)

(b)

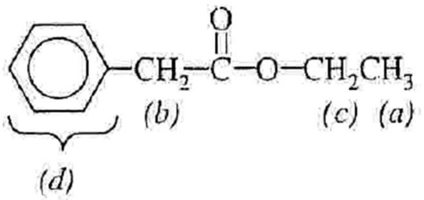


Interpretation:

(a) Doublet δ 1.0 (6H)
(b) Multiplet δ 2.1 (1H)
(c) Doublet δ 4.1 (2H)
(d) Multiplet δ 7.8 (5H)



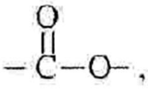
$-\overset{O}{\overset{\|}{C}}-O-$, 1720 cm^{-1} (ester)

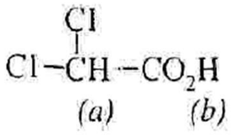
(c) 

$C_6H_5-CH_2-C(=O)-O-CH_2CH_3$

Interpretation:

(*a*) Triplet δ 1.2 (3H)
(*b*) Singlet δ 3.5 (2H)
(*c*) Quartet δ 4.1 (2H)
(*d*) Multiplet δ 7.3 (5H)

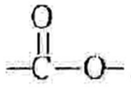

$-\overset{O}{\overset{\|}{C}}-O-$, 1740 cm^{-1} (ester)

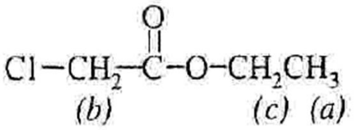
(d) 

$Cl-\overset{Cl}{\overset{|}{C}}H-CO_2H$

Interpretation: —OH , 2500-2700 cm^{-1}

(*a*) Singlet δ 6.0
(*b*) Singlet δ 11.7

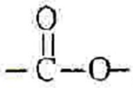

$-\overset{O}{\overset{\|}{C}}-O-$, 1705 cm^{-1} (acid)

(e) 

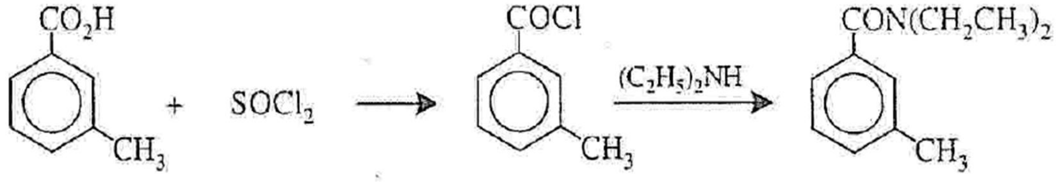
$Cl-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3$

Interpretation:

(*a*) Triplet δ 1.3
(*b*) Singlet δ 4.0
(*c*) Quartet δ 4.2


$-\overset{O}{\overset{\|}{C}}-O-$, 1745 cm^{-1} (ester)

18.37 *N,N*-Dietil-*m*-toluamit, *m*-$CH_3C_6H_4CON(CH_2CH_3)_2$ böcek kovucu bir maddedir. *m*-Toluik asitten başlayarak bu maddenin sentezini gösteriniz?

18.37 

18.38 Amitler karşılık geldikleri aminlerden daha zayıf bazdırlar. Örneğin, suda çözünmeyen birçok amin (RNH_2) seyreltik sulu asitler (sulu HCl, H_2SO_4 gibi) içerisinde alkilamonyum tuzları ($RNH_3{}^+X^-$) oluşturarak çözünür. Onlara karşılık gelen amitler ($RCONH_2$) ise *seyreltik sulu asitlerde çözünmezler*. Buna göre, amitlerin aminlere oranla çok daha zayıf baz oluşlarını açıklayınız.

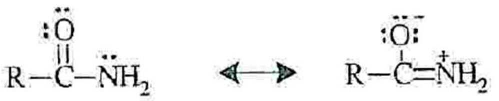
18.38 Alkyl groups are electron releasing; they help disperse the positive charge of an alkylammonium salt and thereby help to stabilize it.

$$R\ddot{N}H_2 + H_3O^+ \longrightarrow R\!\rightarrow\!NH_3^+ + H_2O$$

Stabilized by electron-releasing alkyl group

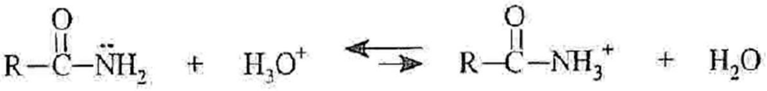
Consequently, alkylamines are somewhat stronger bases than ammonia.

Amides, on the other hand, have acyl groups, $R-\overset{O}{\overset{\|}{C}}-$, attached to nitrogen, and acyl groups are electron withdrawing. They are especially electron withdrawing because of resonance contributions of the kind shown here,



$$R-\overset{:\ddot{O}}{\overset{\|}{C}}-\ddot{N}H_2 \longleftrightarrow R-\overset{:\ddot{O}:^-}{\overset{|}{C}}=\overset{+}{N}H_2$$

This kind of resonance also *stabilizes* the amide. The tendency of the acyl group to be electron withdrawing, however, *destabilizes* the conjugate acid of an amide, and reactions such as the following do not take place to an appreciable extent.



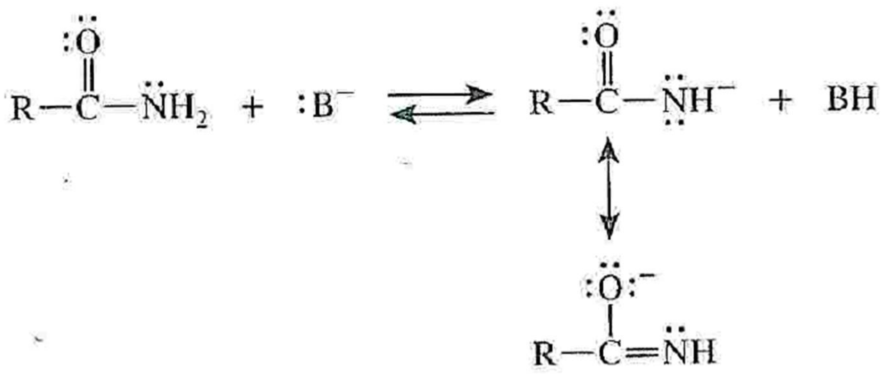
$$R-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2 + H_3O^+ \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-NH_3^+ + H_2O$$

Stabilized by resonance

Destabilized by electron-withdrawing acyl group

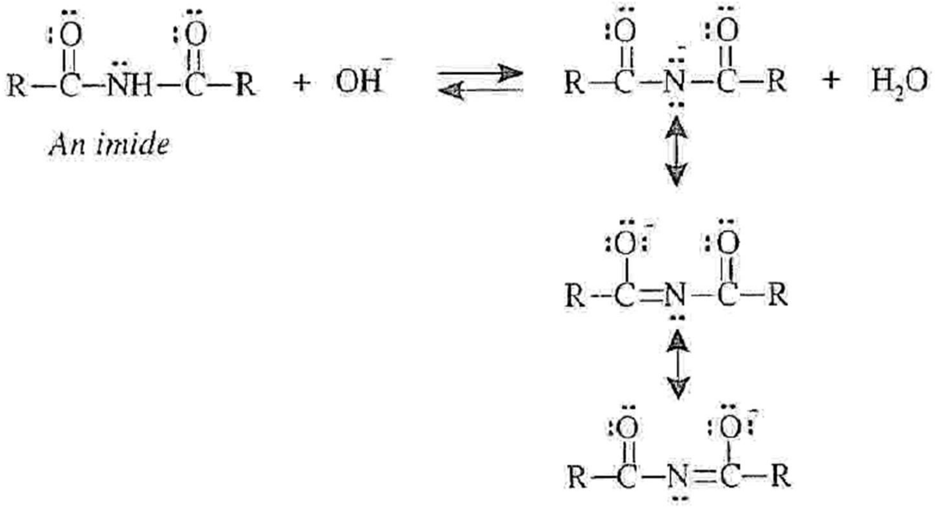
18.39 Amitler aminlerden daha az bazik fakat daha kuvvetli asitlerdir. Amitlerin pK_a değerleri 14-16 arasındadır. Aminlerin pK_a'sı ise 33-35 aralığındadır. **(a)** Amitlerin çok daha kuvvetli olan asitlikleri hangi etkenlere bağlıdır? **(b)** İmitler $(R\overset{O}{\overset{\|}{C}})_2NH$ yapısındadır ve amitlerden daha kuvvetli asitlerdir. İmitlerin pK_a değerleri 9-10'dur ve suda çözünmemelerine karşılık sulu NaOH içerisinde sodyum tuzları oluşturarak çözünürler. İmitlerin daha fazla asidik oluşunu hangi ek etken açıklar?

18.39 (a) The conjugate base of an amide is stabilized by resonance.

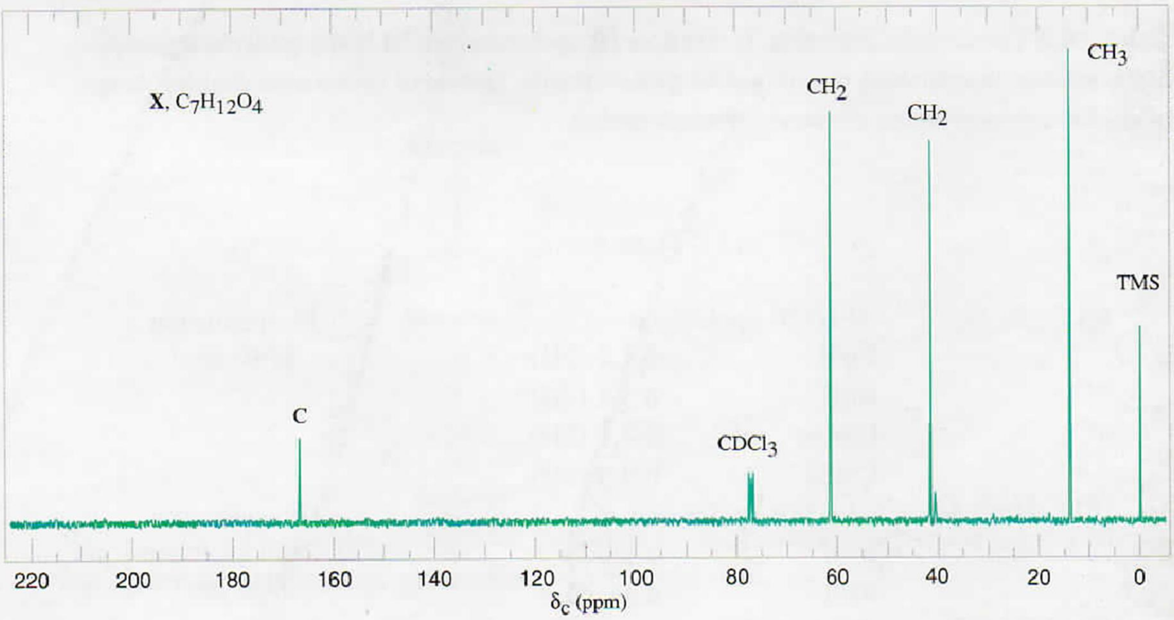


This structure is especially stable because the negative charge is on oxygen.

(b) The conjugate base of an imide is stabilized by an additional resonance structure.



18.40 **X** Bileşiği ($C_7H_{12}O_4$), sulu sodyum bikarbonat içerisinde çözünmez. **X**'in İR spektrumu 1740 cm^{-1}'de kuvvetli bir soğurma piki verir, ve ^{13}C NMR spektrumu Şekil 18.6'da verilmiştir. **X**'in yapısı nedir?

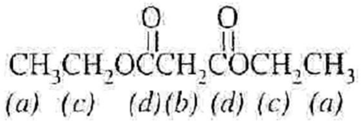


Şekil 18.6 **Problem 18.40'da verilen X bileşiğinin genişband proton-eşleşmesiz ^{13}C NMR spektrumu. DEPT ^{13}C NMR spektrumdan elde edilen bilgiler her bir pik üzerinde verilmiştir.**

18.40 That compound **X** does not dissolve in aqueous sodium bicarbonate indicates that **X** is not a carboxylic acid. That **X** has an IR absorption peak at 1740 cm^{-1} indicates the presence of a carbonyl group, probably that of an ester (Table 18.5). That the molecular formula of **X** ($C_7H_{12}O_4$) contains four oxygen atoms suggests that **X** is a diester.

The ^{13}C spectrum shows only four signals indicating a high degree of symmetry for **X**. The single signal at δ 166.7 is that of an ester carbonyl carbon, indicating that both ester groups of **X** are equivalent.

Putting these observations together with the information gathered from DEPT ^{13}C spectra and the molecular formula leads us to the conclusion that **X** is diethyl malonate. The assignments are

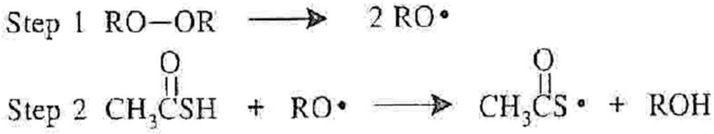


$$\underset{(a)}{CH_3}\underset{(c)}{CH_2}O\underset{(d)}{\overset{O}{\overset{\|}{C}}}\underset{(b)}{CH_2}\underset{(d)}{\overset{O}{\overset{\|}{C}}}O\underset{(c)}{CH_2}\underset{(a)}{CH_3}$$

(*a*) δ 14.2
(*b*) δ 41.6
(*c*) δ 61.3
(*d*) δ 166.7

18.41 Alkiltiyo asetatlar $\left(CH_3\overset{O}{\overset{\|}{C}}SCH_2CH_2R\right)$, tiyolasetik asit $\left(CH_3\overset{O}{\overset{\|}{C}}SH\right)$ ve bir alkenin ($CH_2{=}CHR$) peroksitle başlatılan bir tepkimesiyle elde edilebilir. **(a)** Bu tepkime için uygun bir mekanizma yazınız. **(b)** Bu tepkimenin, 2-metil-2-bütenden 3-metil-2-bütantiyolün sentezinde nasıl kullanılabileceğini gösteriniz.

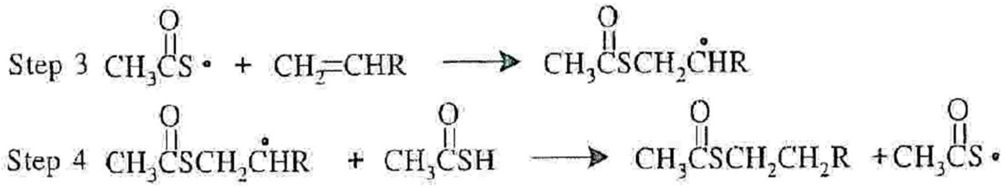
18.41 (a) ***Chain Initiation***



Step 1 $RO{-}OR \longrightarrow 2\,RO\cdot$

Step 2 $CH_3\overset{O}{\overset{\|}{C}}SH + RO\cdot \longrightarrow CH_3\overset{O}{\overset{\|}{C}}S\cdot + ROH$

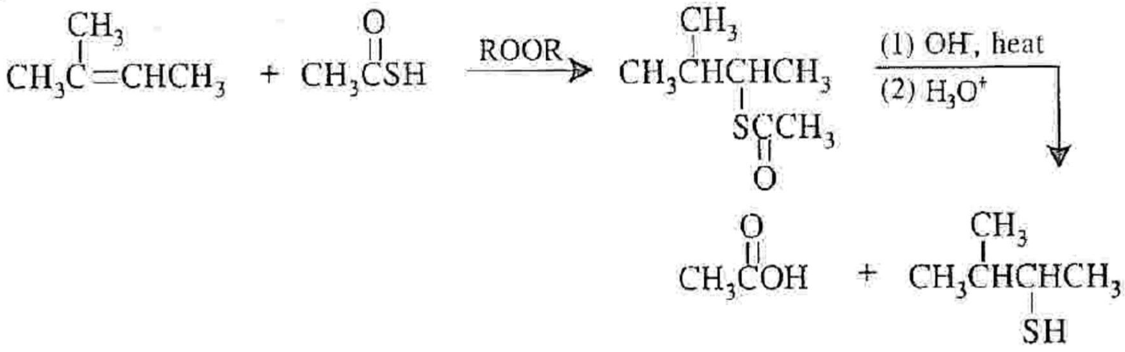
Chain Propagation



Step 3 $CH_3\overset{O}{\overset{\|}{C}}S\cdot + CH_2{=}CHR \longrightarrow CH_3\overset{O}{\overset{\|}{C}}SCH_2\dot{C}HR$

Step 4 $CH_3\overset{O}{\overset{\|}{C}}SCH_2\dot{C}HR + CH_3\overset{O}{\overset{\|}{C}}SH \longrightarrow CH_3\overset{O}{\overset{\|}{C}}SCH_2CH_2R + CH_3\overset{O}{\overset{\|}{C}}S\cdot$

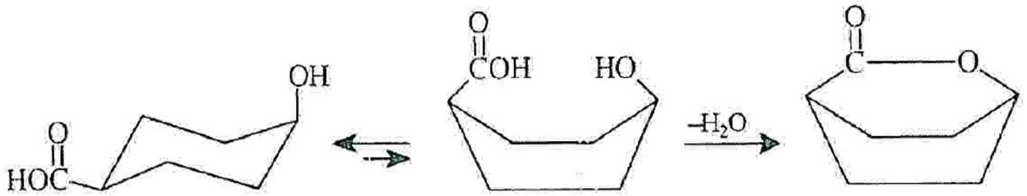
(b)



$$CH_3\underset{}{\overset{CH_3}{\overset{|}{C}}}{=}CHCH_3 + CH_3\overset{O}{\overset{\|}{C}}SH \xrightarrow{ROOR} CH_3\overset{CH_3}{\overset{|}{C}}H\underset{\underset{\underset{O}{\|}}{SCCH_3}}{\underset{|}{C}}HCH_3 \xrightarrow[(2)\ H_3O^+]{(1)\ OH^-,\ heat} CH_3\overset{O}{\overset{\|}{C}}OH + CH_3\overset{CH_3}{\overset{|}{C}}H\underset{\underset{SH}{|}}{C}HCH_3$$

18.42 *cis*-4-Hidroksisikloheksankarboksilik asitin ısıtılmasıyla bir lakton oluşur, fakat, *trans*-4-hidroksisikloheksankarboksilik asit bu tepkimeyi vermez, niçin? Açıklayınız.

18.42 *cis*-4-Hydroxycyclohexanecarboxylic acid can assume a boat conformation that permits lactone formation.



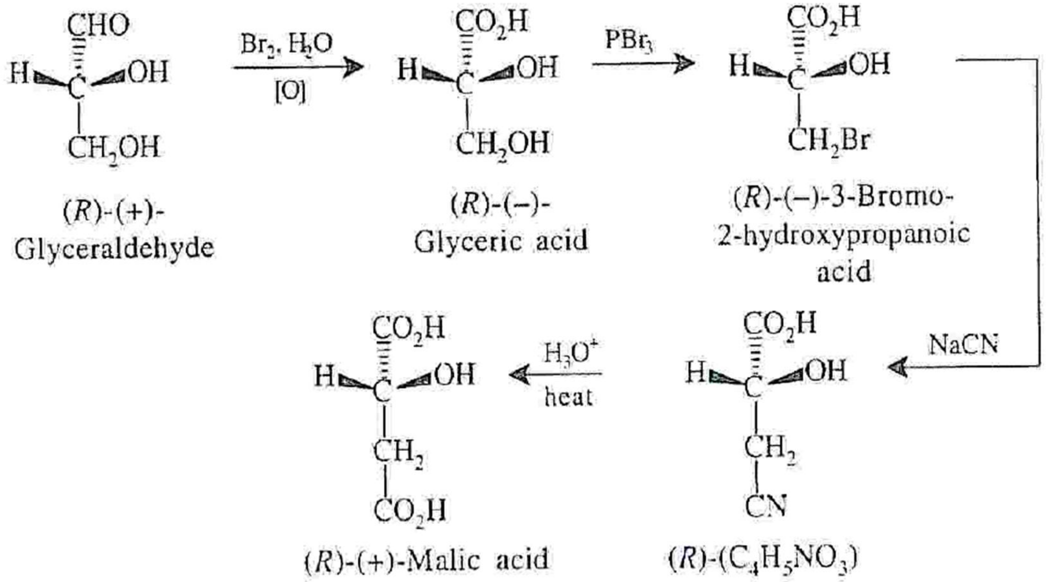
Neither of the chair conformations nor the boat form of *trans*-4-hydroxycyclohexanecarboxylic acid places the –OH group and the $-CO_2H$ group close enough together to permit lactonization.

18.43 (*R*)-(+)-Gliseraldehit, aşağıdaki sentetik yolla (+)-malik asite dönüştürülebilir. Her bir basamaktaki ürünlerin stereokimyasal yapılarını yazınız.

$$(R)\text{-}(+)\text{-Gliseraldehit} \xrightarrow[\text{yükseltgeme}]{Br_2,\ H_2O} (-)\text{-gliserik asit} \xrightarrow{PBr_3}$$

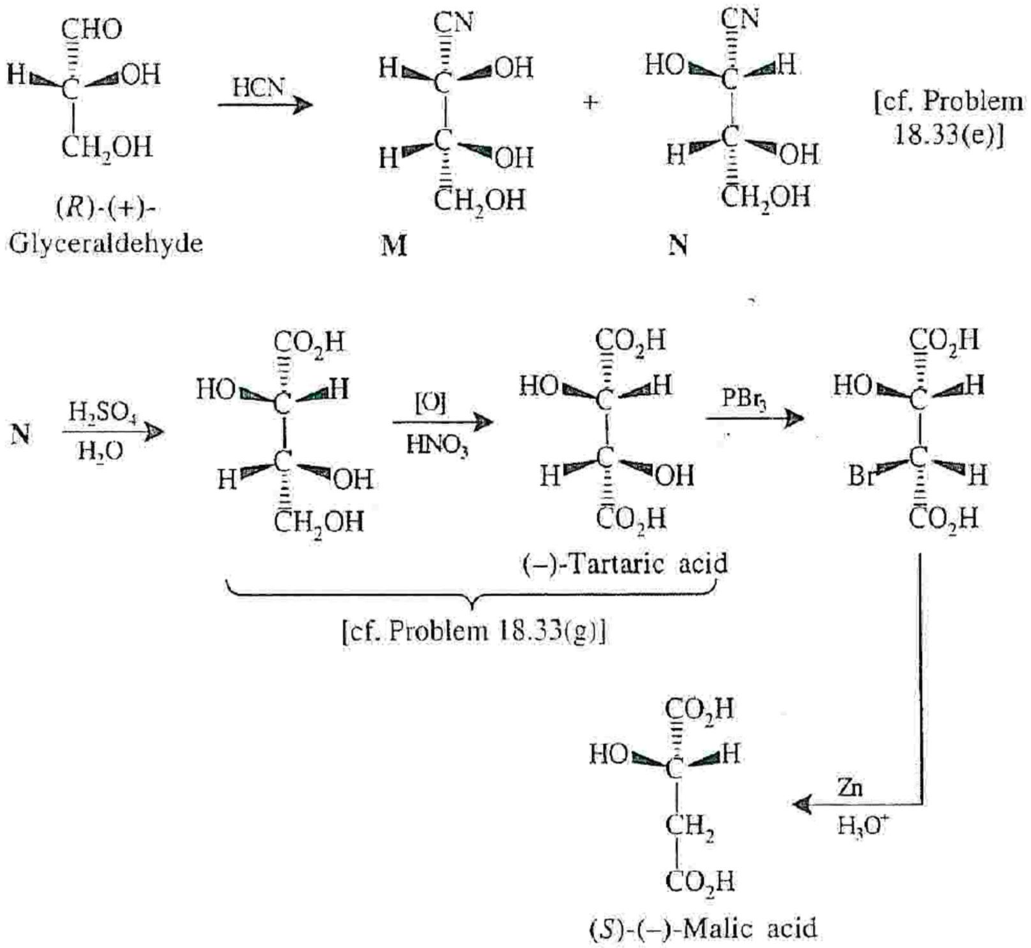
$$(-)\text{-3-bromo-2-hidroksipropanoik asit} \xrightarrow{NaCN} C_4H_5NO_3 \xrightarrow[\text{ısı}]{H_3O^+} (+)\text{-malik asit}$$

18.43

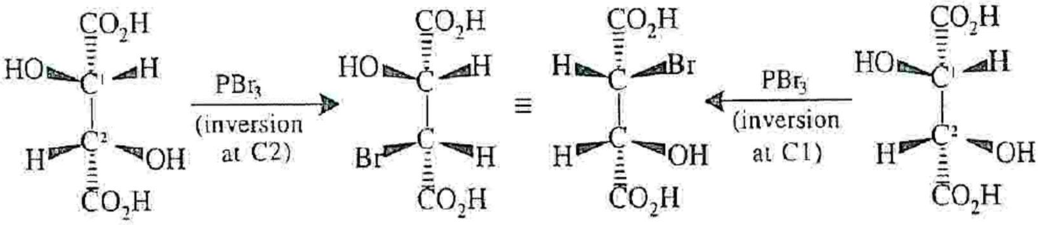


18.44 (*R*)-(+)-Griseraldehit (–)-malik asite de dönüştürülebilir. Bu sentez Problem 18.33'teki (e) ile (g) şıkları; (R)-(+)-gliseraldehitin (–)-tartarik asite dönüşümü ile başlar. Daha sonra (–)-tartarik asit fosfor tribromürle tepkimeye sokularak bir alkolik —OH grubunun —Br grubuyla yer değiştirmesi sağlanır. Bu basamak atağa uğrayan karbon atomu üzerinde konfigurasyonun devrilmesi ile sonuçlanır. Bu tepkimede oluşan ürünün çinko ve asitle etkileştirilmesi sonucu (–)-malik asit oluşur. **(a)** Bu tepkimelerin bütün basamaklarındaki her bir ara ürünün stereokimyasal yapılarını gösteriniz. **(b)** (–)-Tartarik asitin fosfor tribromür ile etkileştirildiği basamakta, iki tane değişebilir —OH olmasına rağmen sadece bir stereoizomer oluşur. Bunun nedenini açıklayınız? **(c)** (–)-Tartarik asitin fosfor tribromür ile etkileştiği basamağın "karışık" stereokimya ile meydana geldiğini varsayalım. Yani atağın olduğu karbon atomunda hem devrilmenin olduğunu hem de konfigurasyonun korunduğunu varsayalım. Bu durumda kaç stereoizomer meydana gelirdi? **(d)** Bu durum tepkimenin sonucunda nasıl bir farklılık meydana getirirdi?

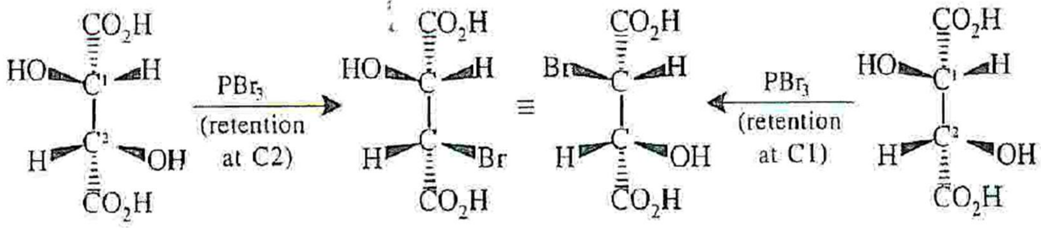
18.44 (a)



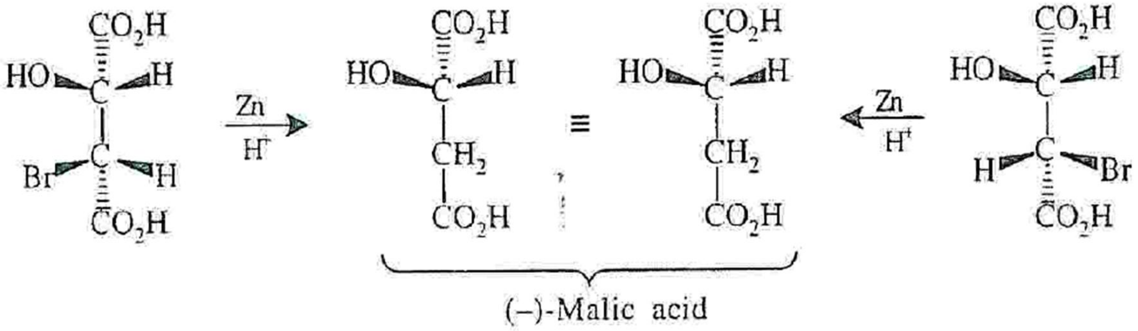
(b) Replacement of either alcoholic –OH by a reaction that proceeds with inversion produces the same stereoisomer.



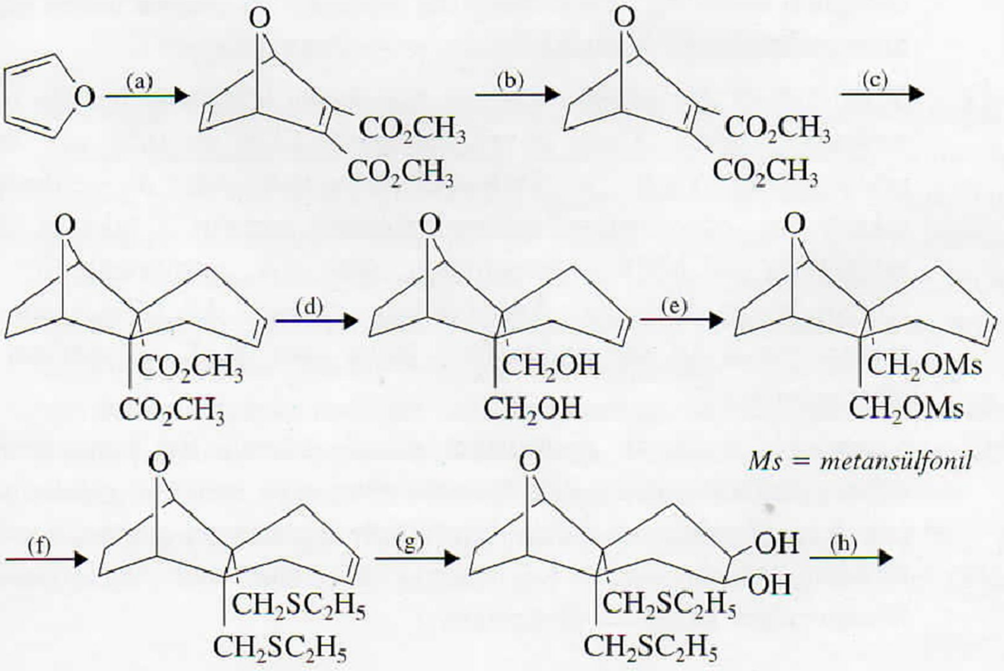
(c) Two. The stereoisomer given in (b) and the one given next, below.



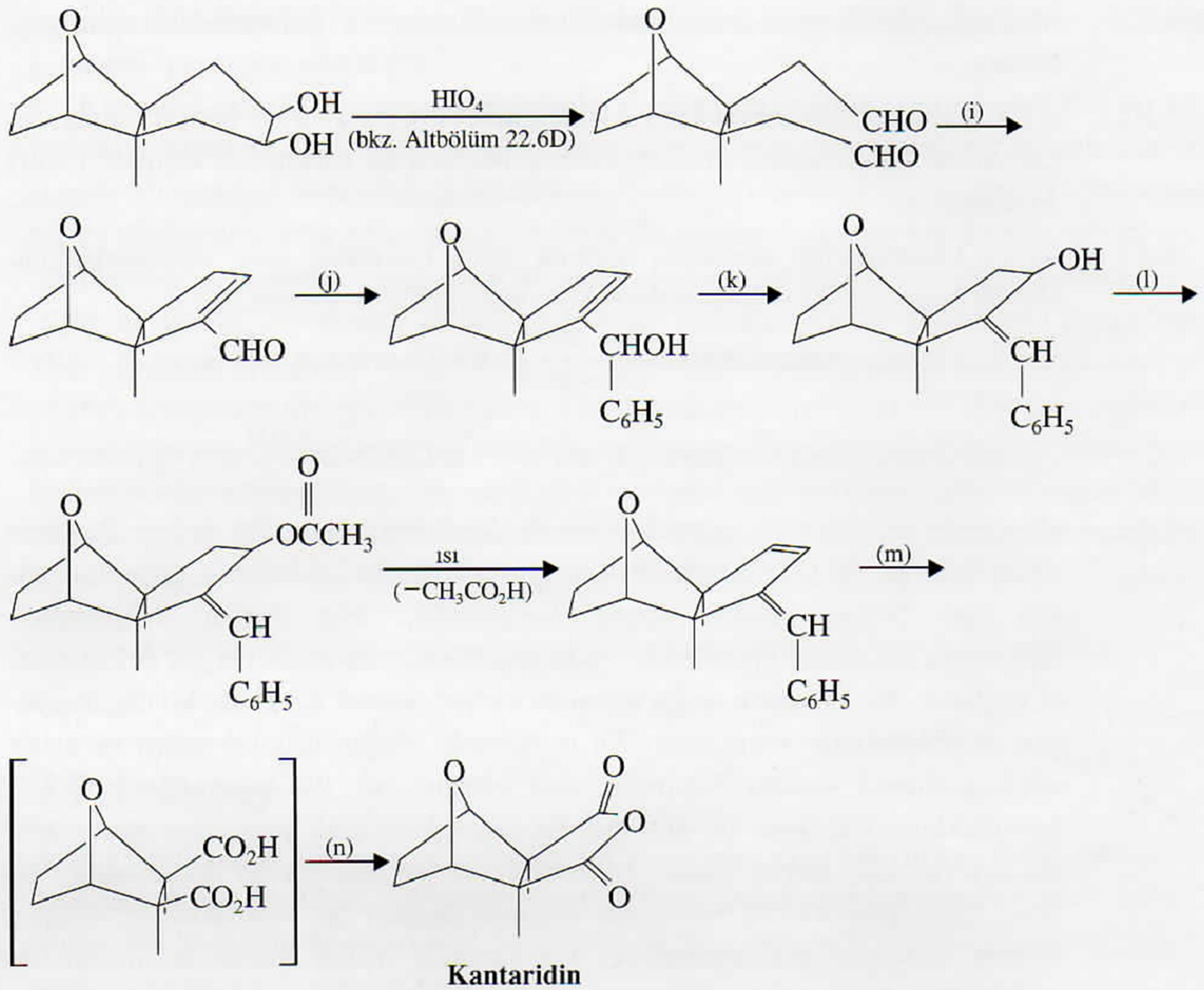
(d) It would have made no difference because treating either isomer (or both together) with zinc and acid produces (−) malic acid.



18.45 Kantaridin deriyi kuvvetli kabartan bir maddedir ve kurutulmuş böceklerden (*Cantharis vesicatoria* veya "İspanyol sineği") izole edilebilir. 1953 yılında Kolombiya Üniversitesinde bulunan Gilbert Stork tarafından kantaridinin stereözgü sentezi yayınlanmıştır. Sentez aşağıda gösterilmiştir. Bu tepkimelerde (a)−(n) arasında verilmeyen reaktifleri yazınız.



Ms = metansülfonil



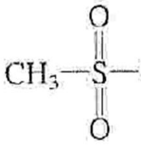
Kantaridin

18.45 (a) $CH_3O_2C-C{\equiv}C-CO_2CH_3$. This is a Diels-Alder reaction.

(b) H_2, Pd. The disubstituted double bond is less hindered than the tetrasubstituted double bond and hence is more reactive.

(c) $CH_2{=}CH-CH{=}CH_2$. Another Diels-Alder reaction.

(d) $LiAlH_4$

(e) 
$CH_3-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-Cl$ and pyridine

(f) $CH_3CH_2S^-$

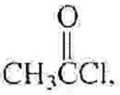
(g) OsO_4

(h) Raney Ni

(i) Base. This is an aldol condensation.

(j) C_6H_5Li (or C_6H_5MgBr) followed by H_3O^+

(k) H_3O^+. This is an acid-catalyzed rearrangement of an allylic alcohol.

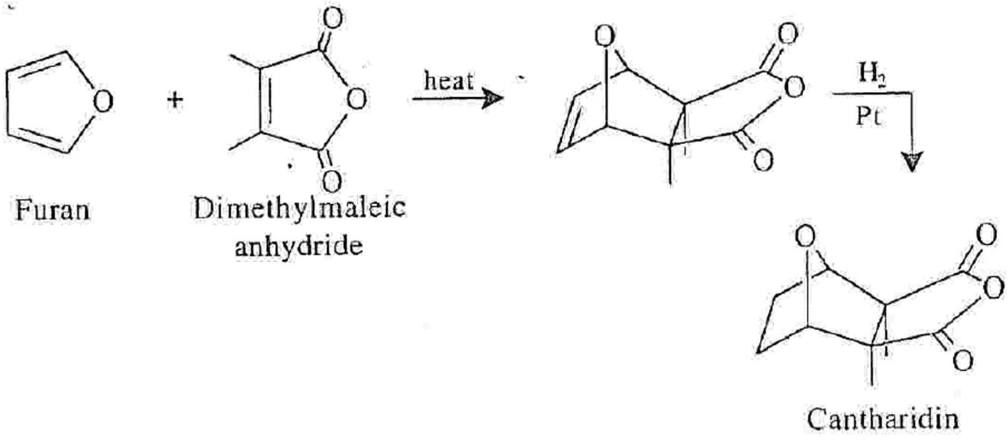
(l) 
$CH_3\overset{\overset{O}{\|}}{C}Cl$, pyridine

(m) O_3, followed by oxidation

(n) Heat

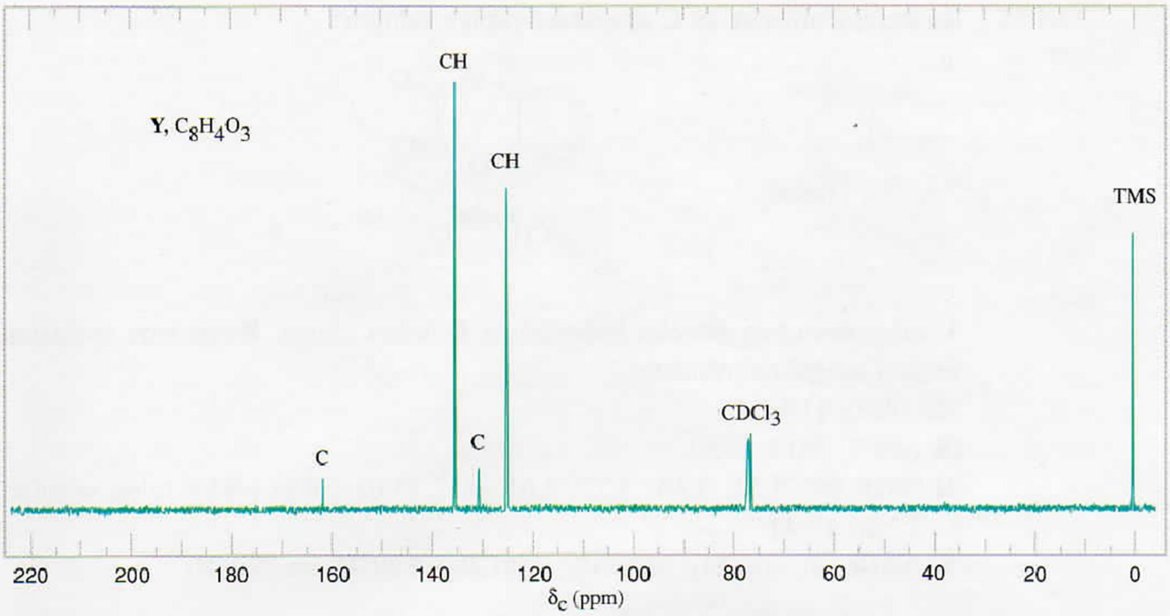
18.46 Kantaridinin yapısını dikkatlice inceleyiniz (Problem 18.45) ve **(a)** furandan (Altbölüm 14.9) başlayarak kantaridin için iki basamaklı olası bir sentez öneriniz. **(b)** 1928 yılında F. von Bruchhausen ve H. W. Bersch, Münster Üniversitesi'nde Diels ve Alder'in yeni bir dien katılmasını açıkladıkları ilk makalelerinin yayınlanmasından yalnızca bir kaç ay sonra bu iki basamaklı sentezi yaptılar ve beklenen katılmanın olmadığını buldular. von Bruchhausen ve H. W. Bersch kantaridinin yüksek sıcaklıklarda kararlı olduğunu da buldular ve kantaridinin palladyum ile ısıtılmasıyla bozunduğunu (parçalandığını) tespit ettiler. Bozunma ürünleri içinde furan ve dimetil maleik anhidritin de olduğunu saptadılar. Bozunmada ne olmuştur? Bozunma neden olabilir? Denenen sentezin ilk basamağı neden gerçekleşmemiştir?

18.46 (a)



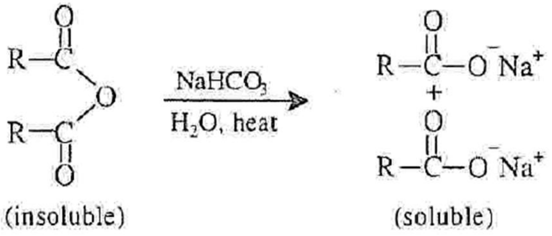
(b) Cantharidin apparently undergoes dehydrogenation to the Diels-Alder adduct shown here, and then the adduct spontaneously decomposes through a reverse Diels-Alder reaction to furan and dimethylmaleic anhydride. These results suggest that the attempted Diels-Alder synthesis fails because the position of equilibrium favors reactants rather than products.

18.47 **Y** Bileşiği ($C_8H_4O_3$) sulu sodyum bikarbonat içerisinde hafifçe ısıtıldığında yavaşça çözünür. **Y**'nin İR spektrumunda 1779 ve 1854 cm^{-1}'de kuvvetli pikler vardır. **Y**'nin ^{13}C NMR spektrumu Şekil 18.7'de verilmiştir. Y'nin bikarbonat çözeltisinin asitlendirilmesi sonucu **Z** bileşiği oluşur. **Z** bileşiğinin ^{13}C NMR spektrumunda dört pik görülmektedir. **Y** etanol içerisinde ısıtıldığında **AA** bileşiği oluşur. **AA** Bileşiğinin ^{13}C NMR spektrumunda 10 pik gözlemiştir. Buna göre **Y, Z,** ve **AA**'nın yapılarını tahmin ediniz.



Şekil 18.7C Problem 18.47'deki Y bileşiğinin genişband proton-eşleşmesiz ^{13}C NMR spektrumu. DEPT ^{13}C NMR spektrumundan elde edilen bilgiler her bir pikin üzerinde gösterilmiştir.

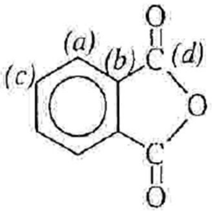
18.47 The very low hydrogen content of the molecular formula of **Y** ($C_8H_4O_3$) indicates that **Y** is highly unsaturated. That **Y** dissolves slowly in warm aqueous $NaHCO_3$ suggests that **Y** is a carboxylic acid anhydride that hydrolyzes and dissolves because it forms a carboxylate salt:



The infrared absorption peaks at 1779 and 1854 cm^{-1} are consistent with those of an aromatic carboxylic anhydride (Table 18.5).

That only four signals appear in the ^{13}C spectrum of **Y** indicates a high degree of symmetry for **Y**. Three of the signals occur in the aromatic region (δ 120–δ 140) and one signal is downfield (δ 163.1)

These signals and the information from the DEPT ^{13}C NMR spectra lead us to conclude that **Y** is phthalic anhydride. The assignments are



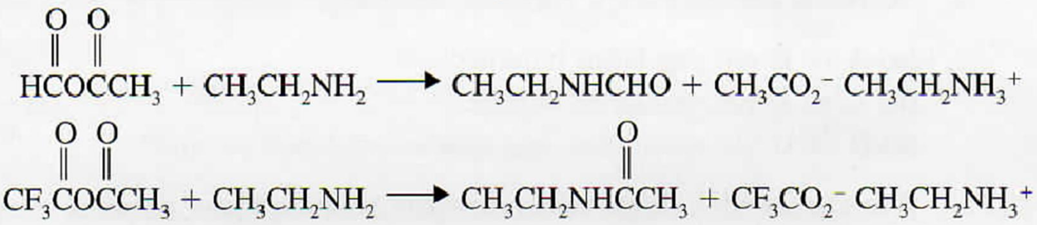
(a) δ 124.3
(b) δ 131.1
(c) δ 136.1
(d) δ 163.1

Z is phthalic acid and **AA** is ethyl hydrogen phthalate.

18.48 Keten, $H_2C{=}C{=}O$, endüstriyel olarak önemli bir kimyasaldır. Asetik asitin yüksek sıcaklıkta dehidrasyonundan veya asetonun pirolizininden elde edilebilir. Ketenin aşağıdaki bileşiklerle tepkimeye girmesi sonucu oluşan ürünleri tahmin ediniz (a) etanol, (b) asetik asit, (c) etilamin (*İpucu:* Markovnikov katılması gerçekleşir.)

18.48 (a) Ethyl acetate (b) Acetic anhydride (c) *N*-Ethylacetamide.

18.49 İki asimetrik anhidrit etilenaminle aşağıdaki gibi tepkimeye girer:



$$H\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3 + CH_3CH_2NH_2 \longrightarrow CH_3CH_2NHCHO + CH_3CO_2^- \; CH_3CH_2NH_3^+$$

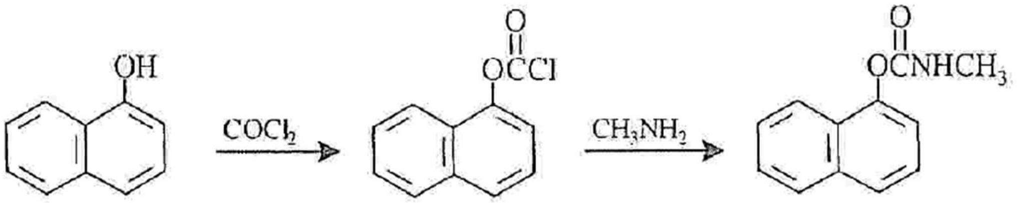
$$CF_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3 + CH_3CH_2NH_2 \longrightarrow CH_3CH_2NH\overset{O}{\overset{\|}{C}}CH_3 + CF_3CO_2^- \; CH_3CH_2NH_3^+$$

Her bir tepkimede meydana gelen ürünlerin nasıl oluştuğunu açıklayınız.

18.49 In the first instance, nucleophilic attack by the amine occurs preferentially at the less hindered carbon of the formyl group. (Recall that aldehydes are more reactive than ketones toward nucleophiles for the same reason.) In the second case, $CF_3CO_2^-$ is a better leaving group than $CH_3CO_2^-$ since the former is the conjugate base of the stronger acid.

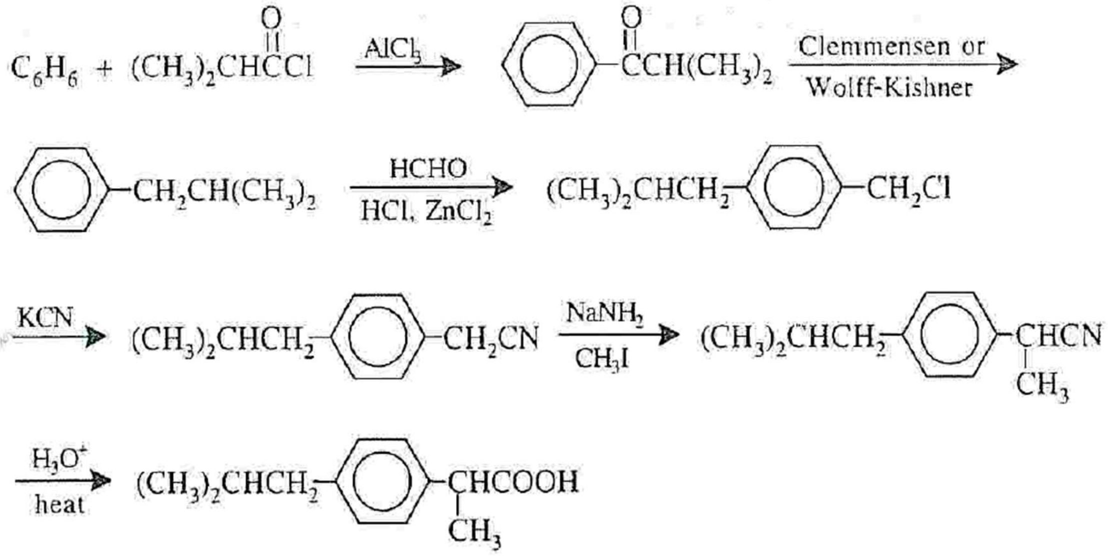
18.50 1-Naftolden başlayarak Altbölüm 18.10A'da gösterilen Sevin adlı haşarat ilacının bir başka sentezini öneriniz.

18.50

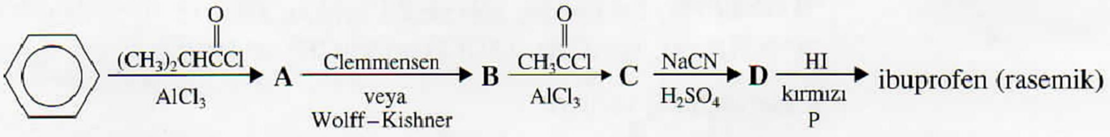


18.51 İbuprofen (Altbölüm 5.10) sentezini benzenden çıkarak, bir basamakta da **klorometilleme** kullanarak yapınız. Klorometilleme tepkimesi Friedel-Crafts tepkimesinin özel bir durumudur; HCHO ve HCl karışımının $ZnCl_2$ içerisindeki bir tepkimesiyle aromatik halkaya —CH_2Cl grubu katılır.

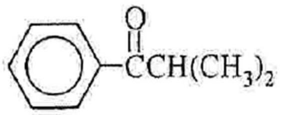
18.51



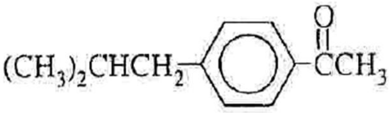
18.52 Aşağıda ibuprofenin alternatif sentezi verilmiştir. **A – D** maddelerinin yapı formüllerini yazınız.



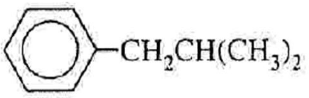
18.52 **A =**



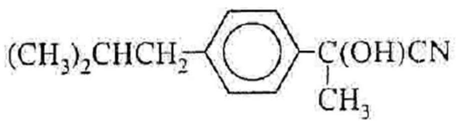
C =



B =



D =



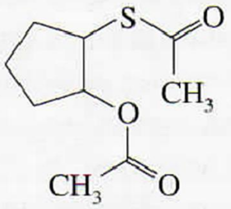
In the last step, HI/red P accomplishes both the reduction of —OH to —H and the hydrolysis of the nitrile function.

18.53 Sinnamaldehit (3-fenil-2-propenal) sentezi için olan bir yöntemde bir kimyacı 3-fenil-2-propen-1-olü sülfürik asit içerisindeki $K_2Cr_2O_7$ ile etkileştirdi. Oluşan ürünün ^{13}C NMR spektrumunda δ 164,5'te bir pik gözlendi. 3-Fenil-2-propen-1-ol, CH_2C1_2 içerisinde PCC ile etkileştirildiğinde ise oluşan ürünün ^{13}C NMR spektrumunda δ 193,3'te bir pik gözükmektedir (her iki maddenin diğer karbon pikleri benzer kimyasal kayma değerine sahiptir.) **(a)** Hangi tepkime sinnamaldehiti oluşturur? **(b)** Diğer ürün nedir?

18.53 (a) The signal at δ 193.8 is consistent with the carbonyl carbon of an aldehyde and shows that the PCC reaction produced cinnamaldehyde.

(b) The signal at δ 164.5 is consistent with the carbonyl carbon of a carboxylic acid, and suggests that the oxidation with $K_2Cr_2O_7$ in sulfuric acid produced cinnamic acid.

***18.54** İki stereoizomer **A** ve **C** aşağıdaki yapıya sahiptir:



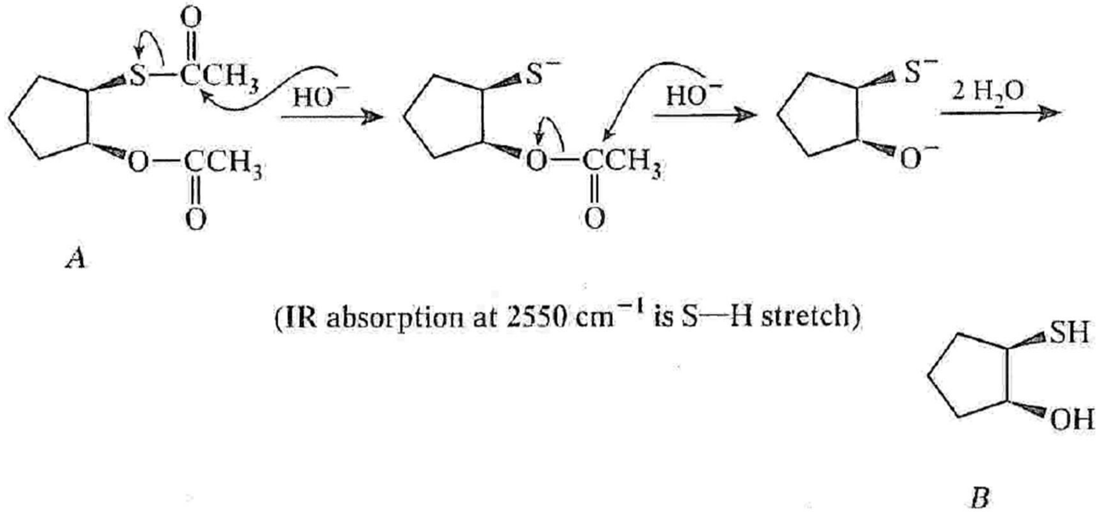
A izomerinin baz destekli hidroliziyle **B** ürünü oluşur. **B**'nin bazı spektrum verileri aşağıda verilmiştir.
MS (m/z): 118 ($M^{+\cdot}$)
IR (cm^{-1}): 3415, 2550
^{1}**H NMR** (δ): 1,51, 1,66; 1,77, 2,65 ve 3,55'da çoklu pikler (alan oranları 2 : 2 : 2 : 1 : 1)
^{13}**C NMR** (δ): 16(CH_2), 28(CH_2), 30(CH_2), 39(CH) ve 77(CH)

Aynı şartlarda **C** izomeri **D** ürününü verir. **D**'nin spektrum verileri aşağıda verilmiştir.

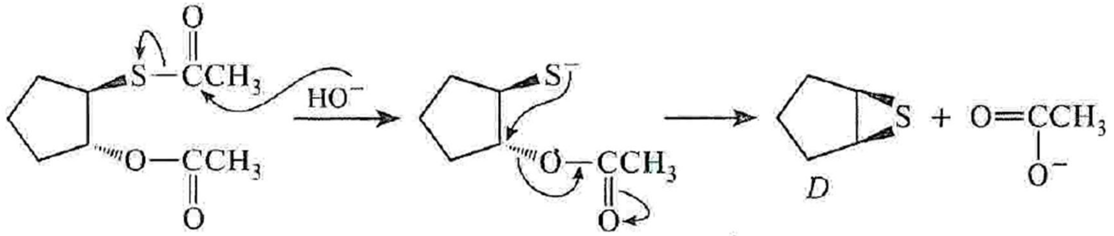
MS (m/z): 100 ($M^{+\cdot}$)
IR (cm^{-1}): 3020
^{1}**H NMR** (δ): 1,51, 1,84 ve 2,25'de çoklu pikler (alan oranları 1 : 2 : 1)
^{13}**C NMR** (δ): 22 (CH_2), 33(CH_2), 35 (CH_2)

(a) A ve **B**'nin yapılarını bulunuz?
(b) C ve **D**'nin yapılarını bulunuz?
(c) B ve **D**'nin oluşumları için mekanizmalarını yazınız?

*18.54

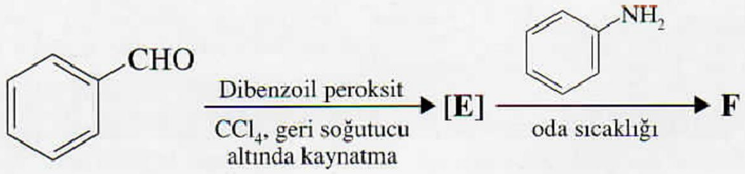


(IR absorption at 2550 cm^{-1} is S—H stretch)



(IR absorption at 3020 cm^{-1} is C—H stretch for C—H of 3-membered ring)

***18.55** **E** ara ürününden (izole edilememiştir) geçerek **F** son ürününü oluşturan aşağıdaki iki basamaklı tepkimeye göz önüne alınız.



E'nin bazı spektrum verileri aşağıda verilmiştir.

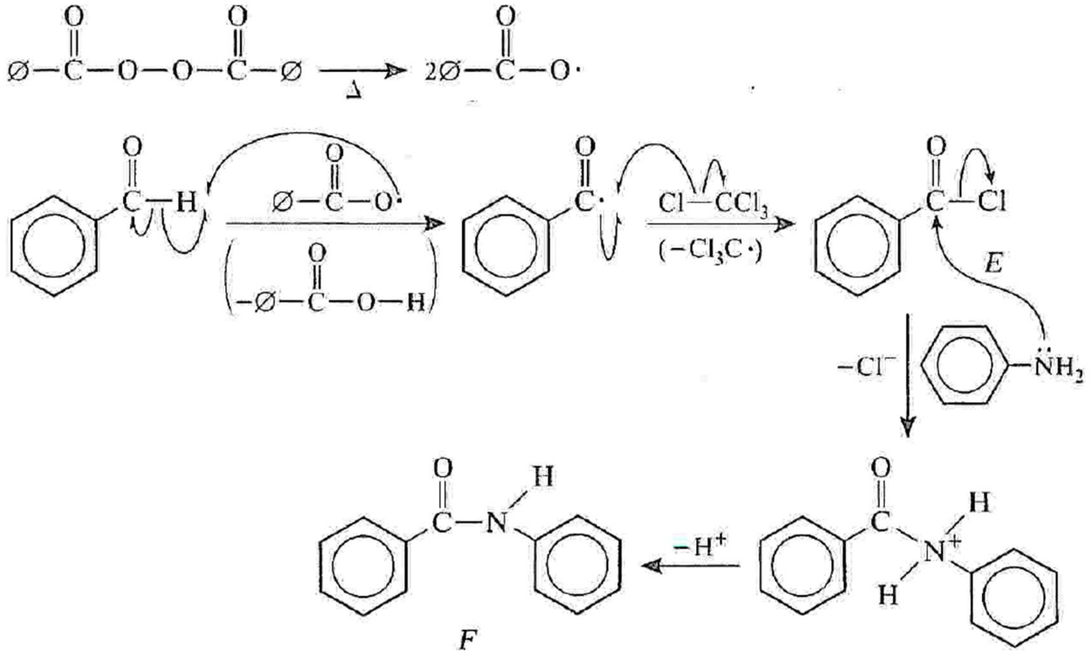
MS (m/z): 105 ($M^{+\cdot}$ değil), 77
IR (cm^{-1}): 3065 (2600'dan 3600'a kadar olan bant), 1774, 1595, 1485, 775, 685
^{1}**H NMR** (δ): 7,6 (çoklu, 3H) ve 8,1 (çoklu, 2H)
^{13}**C NMR** (δ): 129(CH), 131(CH), 133(CH) ve 168(C)

F nin seçilmiş verileri:

MS (m/z): 197 ($M^{+\cdot}$)
IR (cm^{-1}): ($CC1_4$ içerisinde): 3200, 3065, 1690, 1530
^{1}**H NMR** (δ): 10,0 (b), 7,9 (ç, 4H), ve 7,3 (ç, 6H)

(a) **E** ve **F**'nin yapılarını bulunuz?
(b) **E** ve **F**'nin oluşumunun mekanizmasını yazınız.

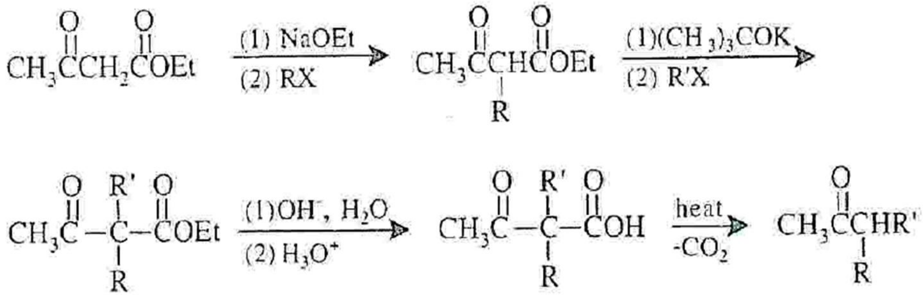
*18.55



β-Dikarbonil Bileşiklerinin Sentezleri ve Tepkimeleri: Enolat Anyonlarıyla İlgili Daha Fazla Kimyasal Bilgi

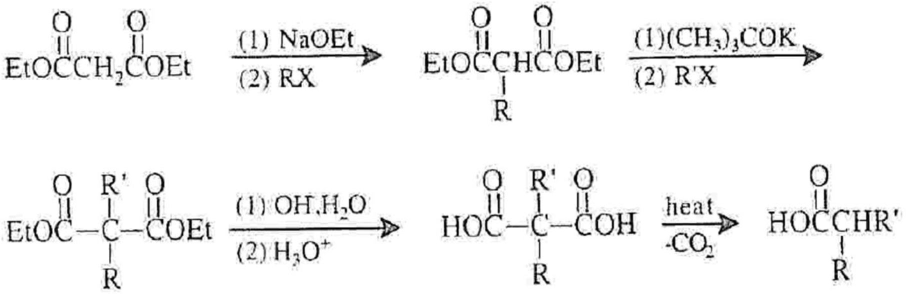
SUMMARY OF ACETOACETIC ESTER AND MALONIC ESTER SYNTHESES

A. Acetoacetic Ester Synthesis



$$\mathrm{CH_3COCH_2COOEt} \xrightarrow[\text{(2) RX}]{\text{(1) NaOEt}} \mathrm{CH_3COCH(R)COOEt} \xrightarrow[\text{(2) R'X}]{\text{(1)(CH}_3)_3\text{COK}} \mathrm{CH_3CO{-}C(R)(R'){-}COOEt} \xrightarrow[\text{(2) H}_3\text{O}^+]{\text{(1)OH}^-,\ \text{H}_2\text{O}} \mathrm{CH_3CO{-}C(R)(R'){-}COOH} \xrightarrow[\text{-CO}_2]{\text{heat}} \mathrm{CH_3COCHR'(R)}$$

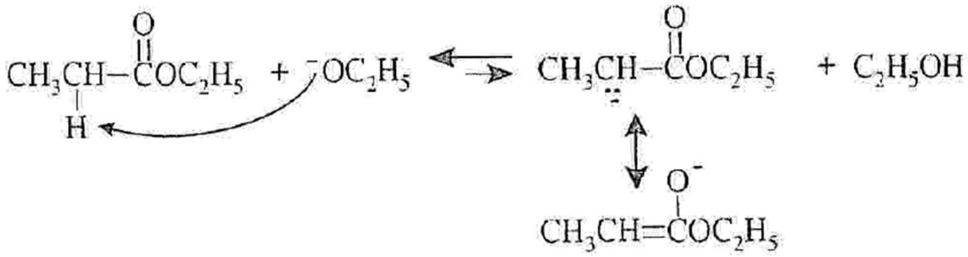
B. Malonic Ester Synthesis



$$\mathrm{EtOCOCH_2COOEt} \xrightarrow[\text{(2) RX}]{\text{(1) NaOEt}} \mathrm{EtOCOCH(R)COOEt} \xrightarrow[\text{(2) R'X}]{\text{(1)(CH}_3)_3\text{COK}} \mathrm{EtOCO{-}C(R)(R'){-}COOEt} \xrightarrow[\text{(2) H}_3\text{O}^+]{\text{(1) OH,H}_2\text{O}} \mathrm{HOCO{-}C(R)(R'){-}COOH} \xrightarrow[\text{-CO}_2]{\text{heat}} \mathrm{HOCOCHR'(R)}$$

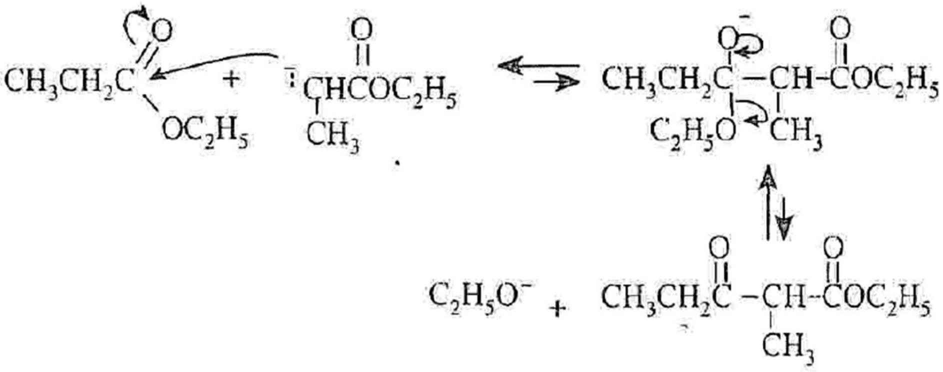
Problem 19.1 ➤ (a) Etil proponoat, etoksit iyonuyla tepkimeye girdiğinde meydana gelen Claisen kondensasyonunun bütün basamaklarının mekanizmasını yazınız. (b) Tepkime karışımı asitlendirildiği zaman hangi ürünler oluşur?

19.1 (a) *Step 1*



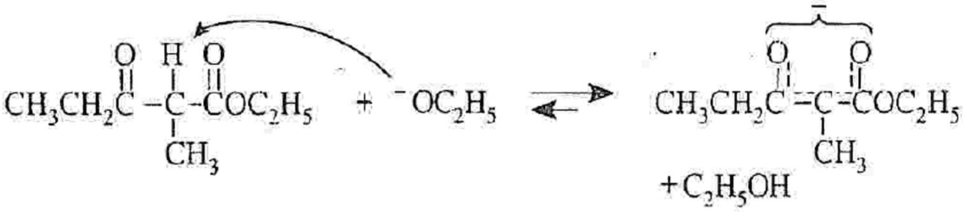
$$CH_3\underset{|}{C}H-\overset{O}{\overset{\|}{C}}OC_2H_5 + {}^-OC_2H_5 \rightleftharpoons CH_3\ddot{C}H-\overset{O}{\overset{\|}{C}}OC_2H_5 + C_2H_5OH \longleftrightarrow CH_3CH=\overset{O^-}{\overset{|}{C}}OC_2H_5$$

Step 2



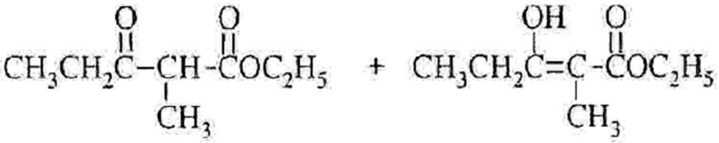
$$CH_3CH_2\overset{O}{\overset{\|}{C}}OC_2H_5 + {}^-\underset{CH_3}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}OC_2H_5 \rightleftharpoons CH_3CH_2\underset{C_2H_5O}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-\underset{CH_3}{\underset{|}{C}}H-\overset{O}{\overset{\|}{C}}OC_2H_5 \rightleftharpoons C_2H_5O^- + CH_3CH_2\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{C}}H-\overset{O}{\overset{\|}{C}}OC_2H_5$$

Step 3



$$CH_3CH_2\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}OC_2H_5 + {}^-OC_2H_5 \rightleftharpoons CH_3CH_2\overset{O}{\overset{|}{C}}=\underset{CH_3}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}OC_2H_5 + C_2H_5OH$$

(b)

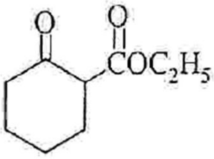


$$CH_3CH_2\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{C}}H-\overset{O}{\overset{\|}{C}}OC_2H_5 + CH_3CH_2\overset{OH}{\overset{|}{C}}=\underset{CH_3}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}OC_2H_5$$

Problem 19.2

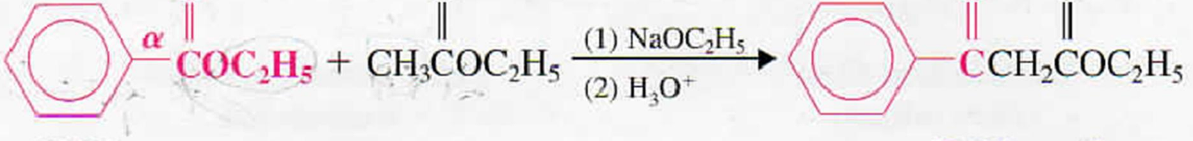
(a) Dietil heptandioatın (dietil pimelat) Dieckmann kondensasyonu sonucu hangi ürünleri elde edersiniz? (b) Dietil pentandioat (dietil gluterat) Dieckmann kondensasyonu vermez, bunun nedenini açıklayınız.

19.2 (a)



(b) To undergo a Dieckmann condensation, diethyl glutarate would have to form a highly strained four-membered ring.

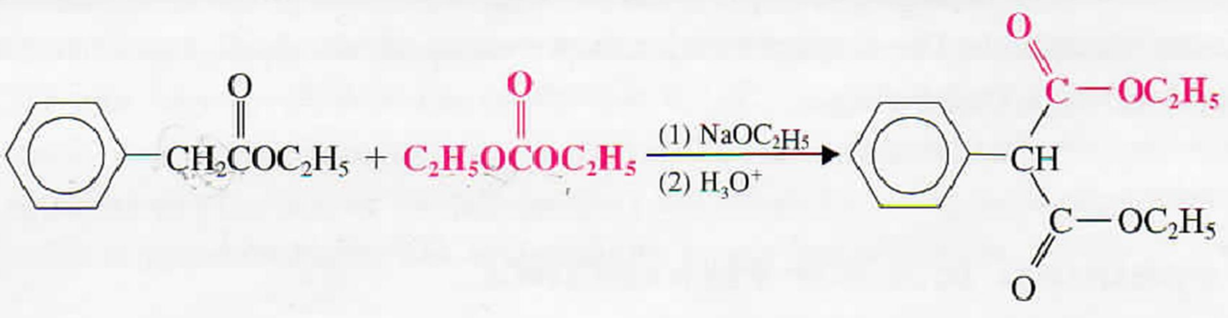
Problem 19.3 Yukarıda verilen iki çapraz Claisen kondensasyon tepkimesinde ürünlerin oluşumunu gösteren tepkime mekanizmalarını yazınız.



$$C_6H_5\overset{O}{\overset{\|}{C}}OC_2H_5 + CH_3\overset{O}{\overset{\|}{C}}OC_2H_5 \xrightarrow[(2)\ H_3O^+]{(1)\ NaOC_2H_5} C_6H_5\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OC_2H_5$$

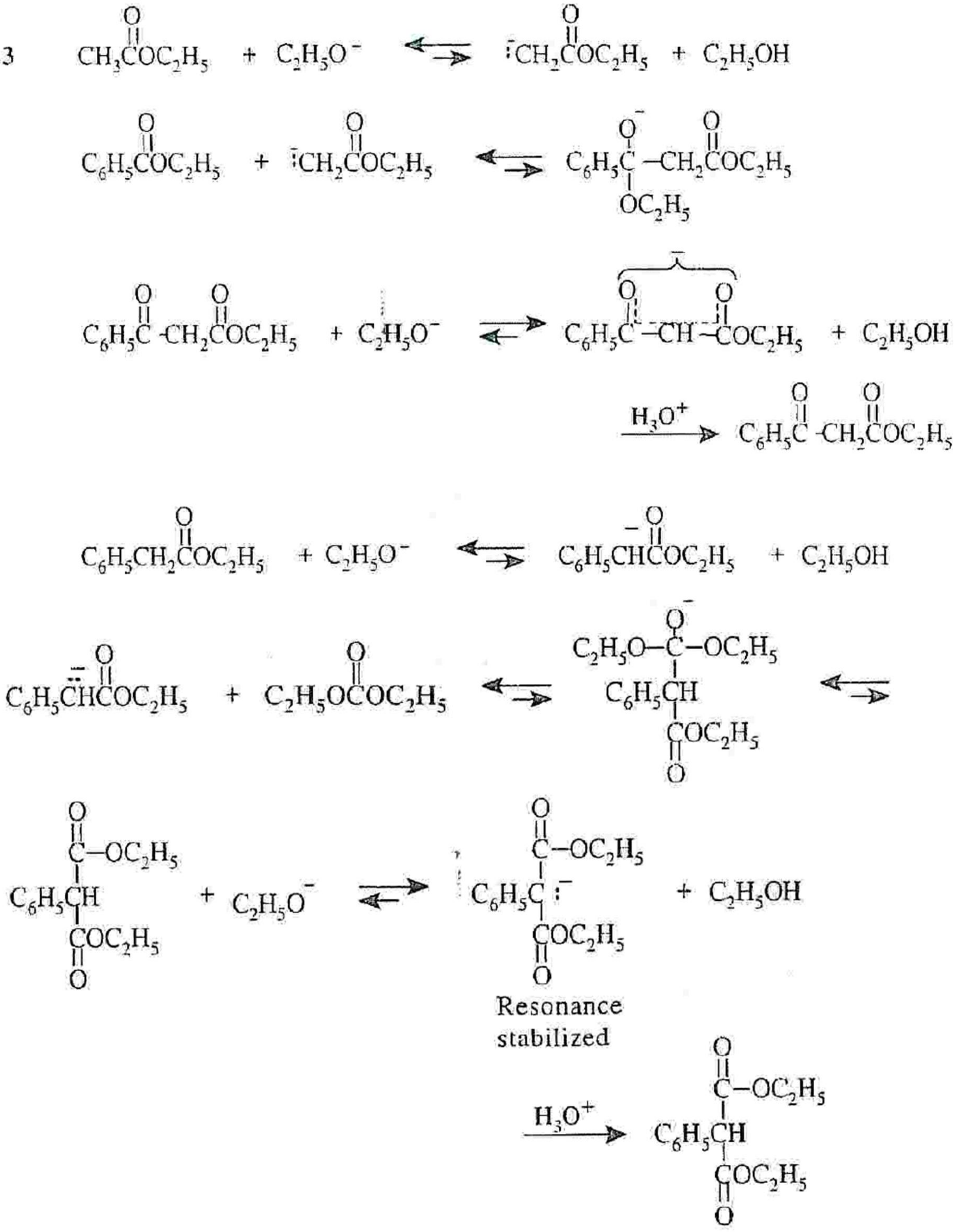
Etil benzoat
(α hidrojeni yok)

Etil benzoilasetat
(%60)



Etil fenilasetat **Dietil karbonat** (α karbonu yok) **Dietil fenilmalonat** (%65)

19.3



$$CH_3\overset{O}{\overset{\|}{C}}OC_2H_5 + C_2H_5O^- \rightleftharpoons {}^{-}\!:CH_2\overset{O}{\overset{\|}{C}}OC_2H_5 + C_2H_5OH$$

$$C_6H_5\overset{O}{\overset{\|}{C}}OC_2H_5 + {}^{-}\!:CH_2\overset{O}{\overset{\|}{C}}OC_2H_5 \rightleftharpoons C_6H_5\underset{OC_2H_5}{\overset{O^-}{C}}-CH_2\overset{O}{\overset{\|}{C}}OC_2H_5$$

$$C_6H_5\overset{O}{\overset{\|}{C}}-CH_2\overset{O}{\overset{\|}{C}}OC_2H_5 + C_2H_5O^- \rightleftharpoons C_6H_5\overset{O}{\overset{\|}{C}}-\overset{-}{C}H-\overset{O}{\overset{\|}{C}}OC_2H_5 + C_2H_5OH \xrightarrow{H_3O^+} C_6H_5\overset{O}{\overset{\|}{C}}-CH_2\overset{O}{\overset{\|}{C}}OC_2H_5$$

$$C_6H_5CH_2\overset{O}{\overset{\|}{C}}OC_2H_5 + C_2H_5O^- \rightleftharpoons C_6H_5\overset{-}{C}H\overset{O}{\overset{\|}{C}}OC_2H_5 + C_2H_5OH$$

$$C_6H_5\overset{..}{\overset{-}{C}}H\overset{O}{\overset{\|}{C}}OC_2H_5 + C_2H_5O\overset{O}{\overset{\|}{C}}OC_2H_5 \rightleftharpoons C_2H_5O-\overset{O^-}{C}(-OC_2H_5)-\underset{\underset{O}{\overset{\|}{C}OC_2H_5}}{C_6H_5CH} \rightleftharpoons$$

$$C_6H_5CH(\overset{O}{\overset{\|}{C}}-OC_2H_5)(\overset{O}{\overset{\|}{C}}OC_2H_5) + C_2H_5O^- \rightleftharpoons C_6H_5\overset{-}{C}\!:(\overset{O}{\overset{\|}{C}}-OC_2H_5)(\overset{O}{\overset{\|}{C}}OC_2H_5) + C_2H_5OH$$

Resonance stabilized

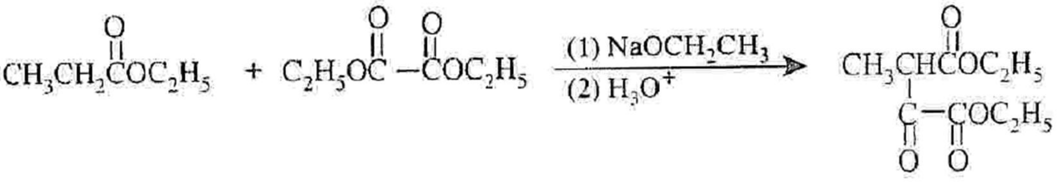
$$\xrightarrow{H_3O^+} C_6H_5CH(\overset{O}{\overset{\|}{C}}-OC_2H_5)(\overset{O}{\overset{\|}{C}}OC_2H_5)$$

Problem 19.4 ➤ Aşağıda verilen çapraz Claisen kondensasyonlarının her birinden oluşmasını beklediğiniz ürünler nelerdir?

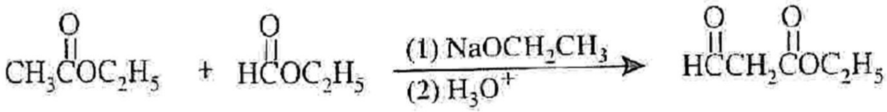
(a) Etilpropanoat + dietil oksalat $\xrightarrow[(2)\ H_3O^+]{(1)\ NaOCH_2CH_3}$

(b) Etil asetat + etil format $\xrightarrow[(2)\ H_3O^+]{(1)\ NaOCH_2CH_3}$

19.4 (a)



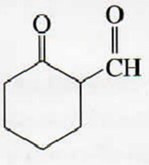
(b)



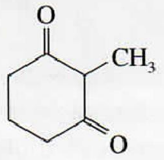
$CH_3\overset{O}{C}OC_2H_5 + H\overset{O}{C}OC_2H_5 \xrightarrow[(2)\ H_3O^+]{(1)\ NaOCH_2CH_3} H\overset{O}{C}CH_2\overset{O}{C}OC_2H_5$

Problem 19.5 ◀ Başlangıç maddeleri olarak esterleri, ketonları, açil halojenürleri vb. seçerek aşağıdaki bileşikleri nasıl sentezlersiniz?

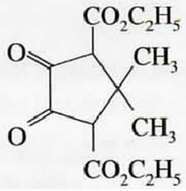
(a)



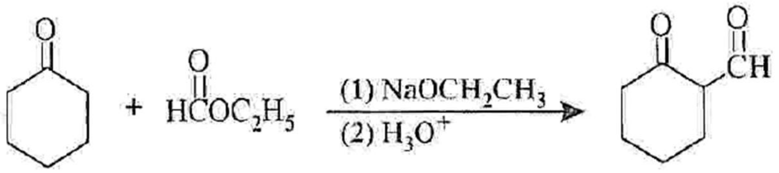
(b)



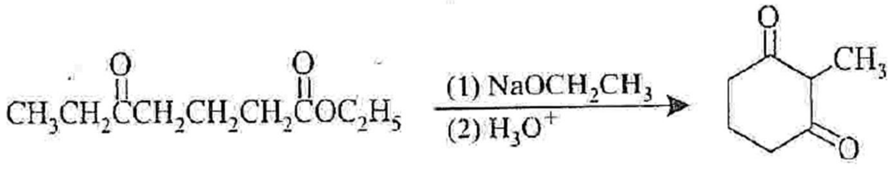
(c)



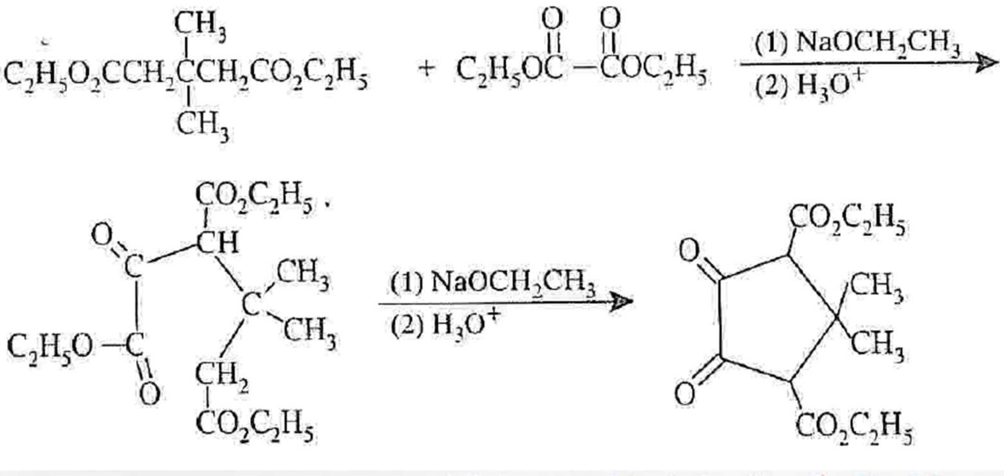
19.5 (a)



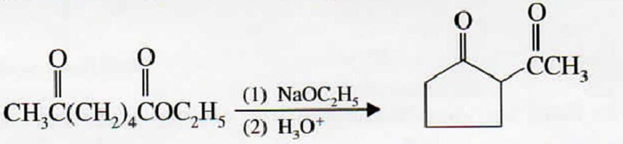
(b)



(c)

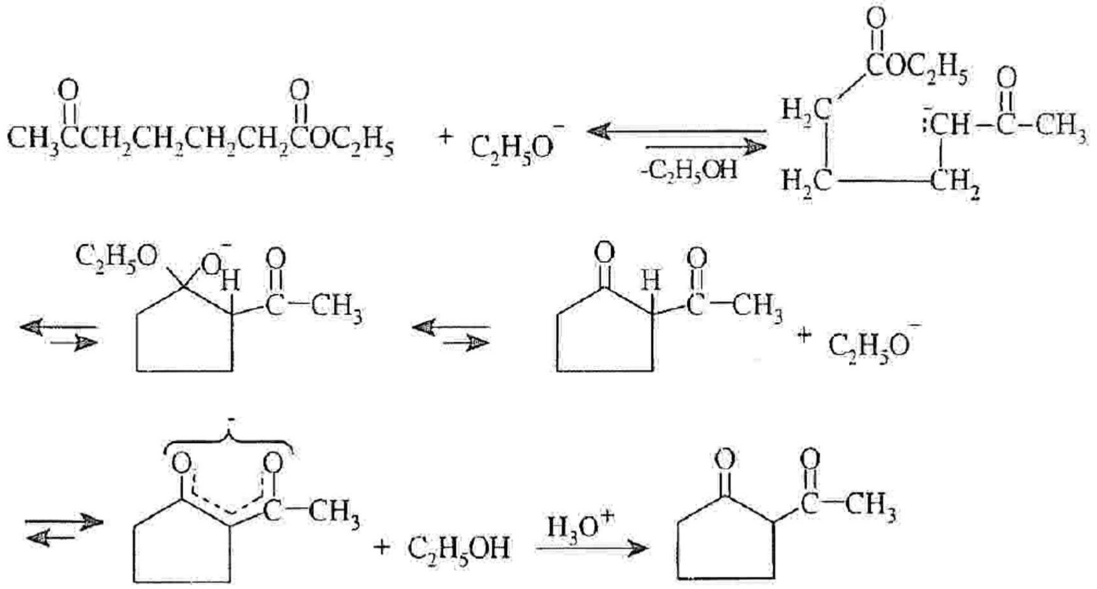


Keto esterler Dieckmann kondenseleşmesine benzer halkalanma tepkimeleri verirler. Aşağıdaki tepkimede oluşan ürünü açıklayan bir mekanizma yazınız. ◀ **Problem 19.6**

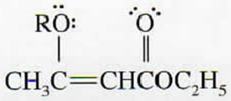


2-Asetilsiklopentanon

19.6



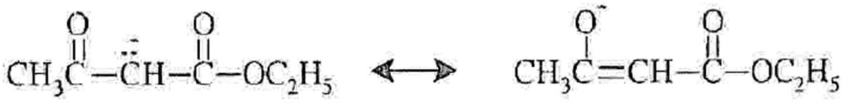
Problem 19.7 ➤ Sodyoasetoasetik esterin alkillenmesinin yan ürünleri, aşağıdaki genel formülle verilen bileşiklerdir.



$$\mathrm{CH_3\overset{R\ddot{O}:}{\overset{|}{C}}{=}CH\overset{\ddot{O}}{\overset{\|}{C}}OC_2H_5}$$

Bunların nasıl oluştuklarını açıklayınız.

19.7 The partially negative oxygen atom of sodioacetoacetic ester acts as the nucleophile.

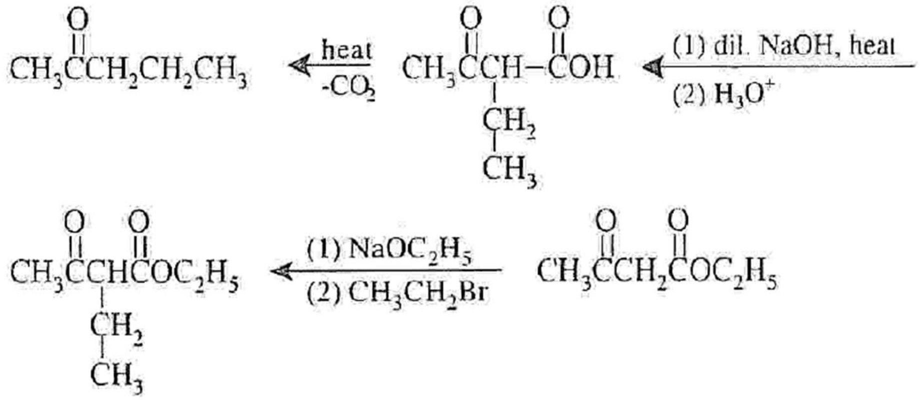


$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}-\overset{-}{\ddot{C}}H-\overset{O}{\overset{\|}{C}}-OC_2H_5} \longleftrightarrow \mathrm{CH_3\overset{O^-}{\overset{|}{C}}{=}CH-\overset{O}{\overset{\|}{C}}-OC_2H_5}$$

Problem 19.8 ➤ Aşağıdaki her bir bileşiği hazırlamak için asetoasetik ester sentezinin nasıl kullanıldığını gösteriniz: (a) 2-pentanon (b) 3-propil-2-heksanon ve (c) 4-fenil-2- bütanon.

19.8 Again, working backward,

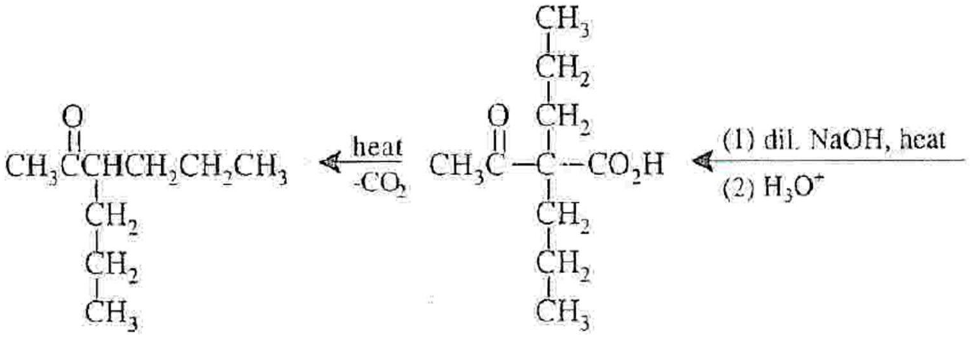
(a)



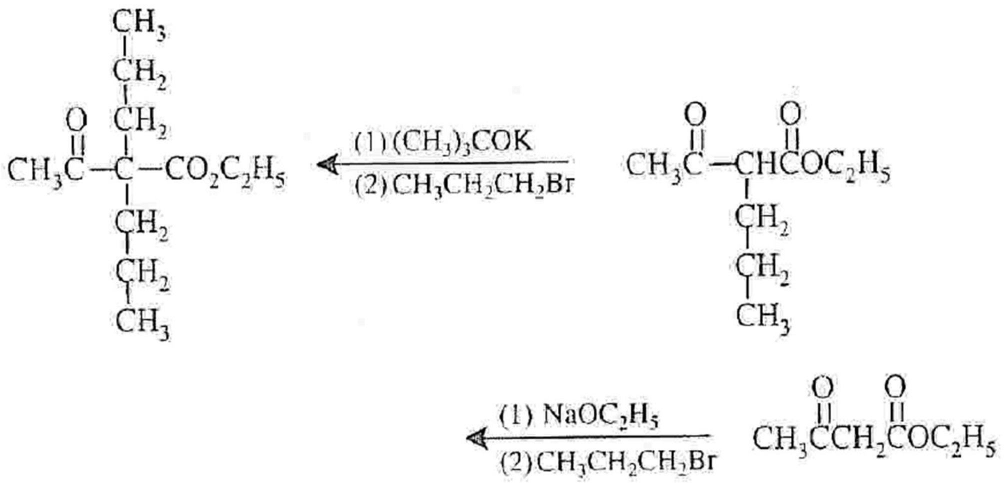
$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3} \xleftarrow[\mathrm{-CO_2}]{\text{heat}} \mathrm{CH_3\overset{O}{\overset{\|}{C}}\underset{\substack{|\\ CH_2\\ |\\ CH_3}}{CH}-\overset{O}{\overset{\|}{C}}OH} \xleftarrow[\text{(2) }\mathrm{H_3O^+}]{\text{(1) dil. NaOH, heat}}$$

$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}\underset{\substack{|\\ CH_2\\ |\\ CH_3}}{CH}\overset{O}{\overset{\|}{C}}OC_2H_5} \xleftarrow[\text{(2) }\mathrm{CH_3CH_2Br}]{\text{(1) }\mathrm{NaOC_2H_5}} \mathrm{CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OC_2H_5}$$

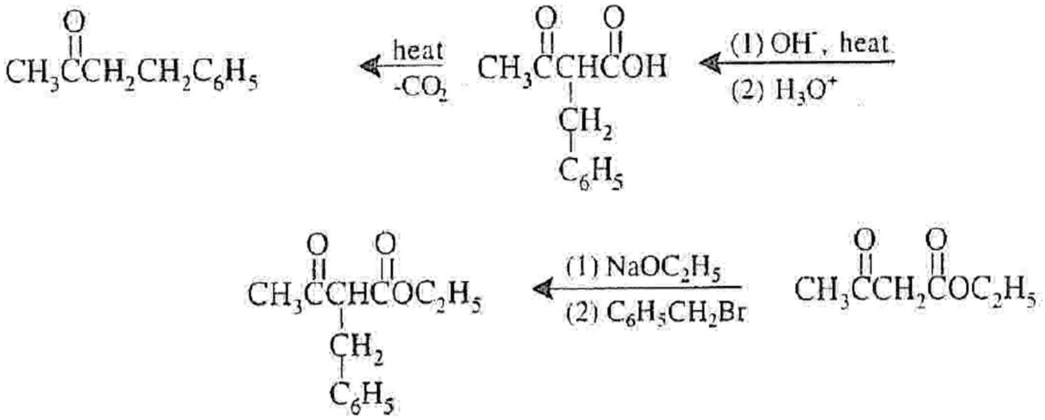
(b)



$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}\underset{\substack{|\\ CH_2\\ |\\ CH_2\\ |\\ CH_3}}{CH}CH_2CH_2CH_3} \xleftarrow[\mathrm{-CO_2}]{\text{heat}} \mathrm{CH_3\overset{O}{\overset{\|}{C}}-\overset{\substack{CH_3\\ |\\ CH_2\\ |\\ CH_2\\ |}}{\underset{\substack{|\\ CH_2\\ |\\ CH_2\\ |\\ CH_3}}{C}}-CO_2H} \xleftarrow[\text{(2) }\mathrm{H_3O^+}]{\text{(1) dil. NaOH, heat}}$$



(c)



Problem 19.9 ➤ Genel olarak asetoasetik ester sentezinde, alkilleme basamağında birincil halojenürler kullanıldığında en iyi verim olur, ikincil halojenürlerle düşük verim gerçekleşir ve üçüncül halojenürler ise uygulamada hiç bir alkilleme ürünü vermez (a) Bunu açıklayınız. (b) Sodyoasetoasetik ester ve *ter*-bütil bromürün tepkimesinden hangi ürünlerin oluşmasını beklersiniz? (c) Yukarıda yeni tanımladığımız yolla yapılan asetoasetik ester sentezinde bromobenzen bir arillendirme reaktifi olarak kullanılamaz. Niçin kullanılamaz?

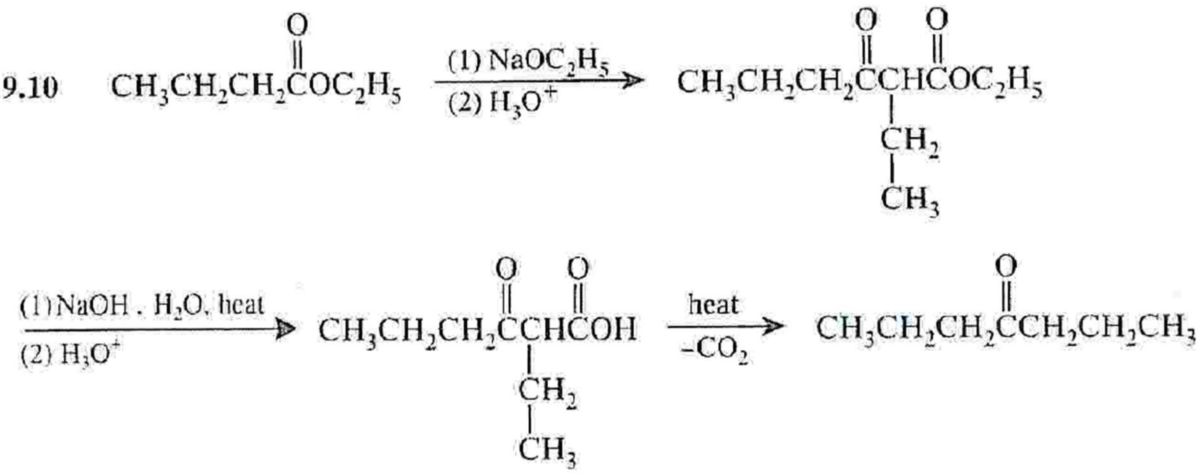
19.9 (a) Reactivity is the same as with any S_N2 reaction. With primary halides substitution is highly favored, with secondary halides elimination competes with substitution, and with tertiary halides elimination is the exclusive course of reaction.

(b) Acetoacetic ester and 2-methylpropene

(c) Bromobenzene is unreactive to nucleophilic substitution.

Problem 19.10 ➤ Claisen kondensasyonu sonucu oluşan ürünler, β-keto esterlerdir. Bu ürünlerin hidrolizi ve dekarboksilasyonu ketonların sentezi için genel bir yöntem verir. 4-Heptanonun sentezinde bu tekniğin nasıl kullanıldığını gösteriniz?

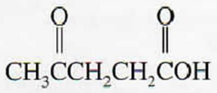
19.10



$$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}OC_2H_5 \xrightarrow[(2)\ H_3O^+]{(1)\ NaOC_2H_5} CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}\underset{\underset{CH_3}{CH_2}}{CH}\overset{O}{\overset{\|}{C}}OC_2H_5$$

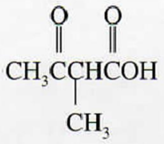
$$\xrightarrow[(2)\ H_3O^+]{(1)\ NaOH,\ H_2O,\ heat} CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}\underset{\underset{CH_3}{CH_2}}{CH}\overset{O}{\overset{\|}{C}}OH \xrightarrow[-CO_2]{heat} CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3$$

Yukarıda verilen keto asidin sentezinde elde edilen dikarboksilik asit özel bir şekilde dekarboksilasyona uğrayarak ◄ **Problem 19.11**



$$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}OH$$

verir.



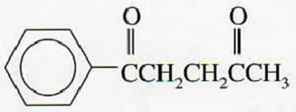
$$CH_3\overset{O}{\overset{\|}{C}}\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}OH$$

elde edilmez.

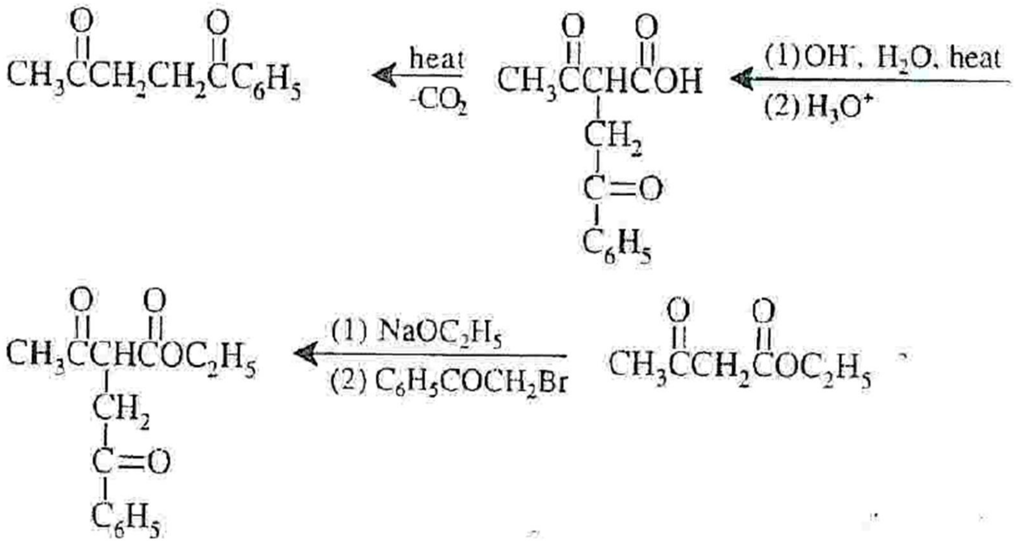
Bu sonucu açıklayınız.

19.11 The carboxyl group that is lost more readily is the one that is β to the keto group (cf. Section 18.11 of the text).

Problem 19.12 ► Aşağıdaki bileşiği hazırlamak için asetoasetik ester sentezini nasıl kullanırsınız?



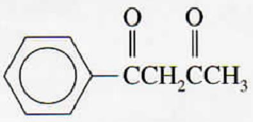
19.12



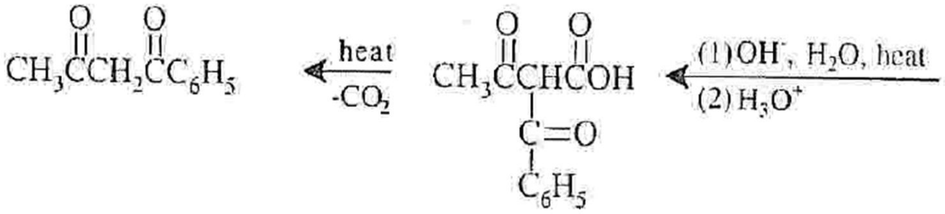
$$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}C_6H_5 \xleftarrow[-CO_2]{heat} CH_3\overset{O}{\overset{\|}{C}}\underset{\underset{\underset{C_6H_5}{C=O}}{CH_2}}{CH}\overset{O}{\overset{\|}{C}}OH \xleftarrow[(2)\ H_3O^+]{(1)\ OH^-,\ H_2O,\ heat}$$

$$CH_3\overset{O}{\overset{\|}{C}}\underset{\underset{\underset{C_6H_5}{C=O}}{CH_2}}{CH}\overset{O}{\overset{\|}{C}}OC_2H_5 \xleftarrow[(2)\ C_6H_5COCH_2Br]{(1)\ NaOC_2H_5} CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OC_2H_5$$

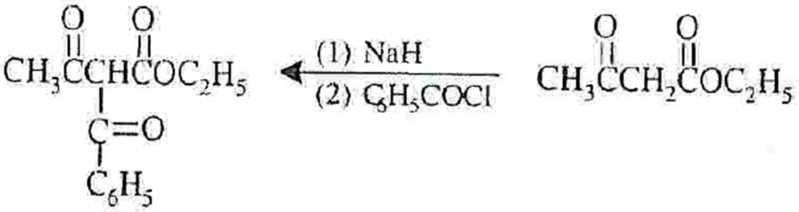
Problem 19.13 ► Aşağıdaki bileşiği asetoasetik ester sentezini kullanarak nasıl sentezlersiniz?



19.13



$$CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}C_6H_5 \xleftarrow[-CO_2]{heat} CH_3\overset{O}{\overset{\|}{C}}\underset{\underset{C_6H_5}{|}}{\underset{C=O}{\underset{|}{C}}}H\overset{O}{\overset{\|}{C}}OH \xleftarrow[(2)\ H_3O^+]{(1)\ OH^-,\ H_2O,\ heat}$$

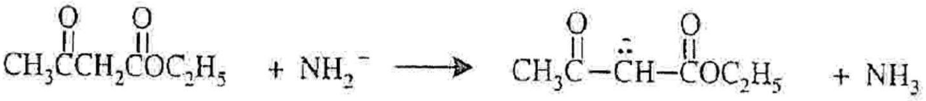


$$CH_3\overset{O}{\overset{\|}{C}}\underset{\underset{C_6H_5}{|}}{\underset{C=O}{\underset{|}{C}}}H\overset{O}{\overset{\|}{C}}OC_2H_5 \xleftarrow[(2)\ C_6H_5COCl]{(1)\ NaH} CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OC_2H_5$$

(a) Asetoasetik esterin bromobenzen ve iki eşdeğer mol sodyum amitle fenillenmesi mekanizmasını basamak basamak gösteriniz. (Niçin iki eşdeğer sodyum amit gerekir?) (b) Fenillenmiş asetoasetik esterin hidrolizi ve dekarboksilasyonu sonucu hangi ürünü elde etmeyi beklersiniz? (c) Fenilasetik asiti malonik esterden nasıl hazırlansınız?

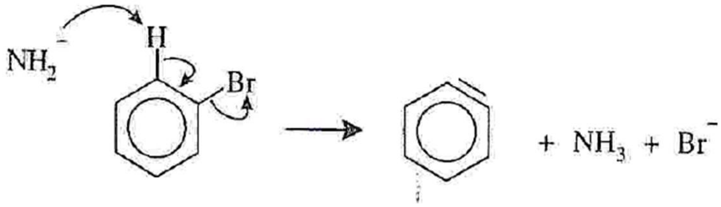
Problem 19.14

19.14 (a) One molar equivalent of $NaNH_2$ converts acetoacetic ester to its anion.

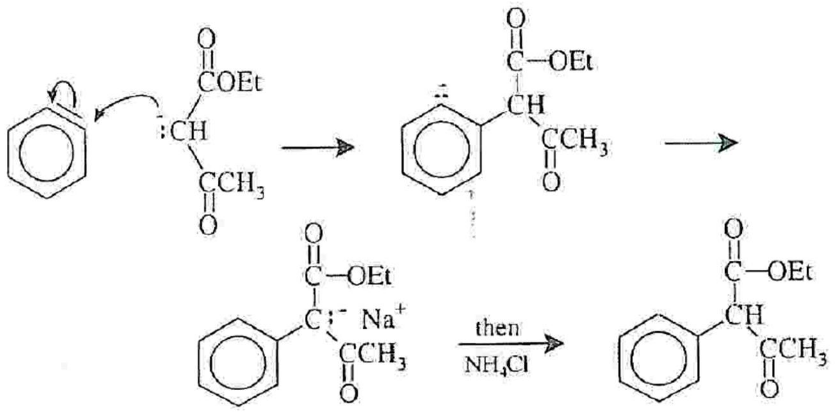


$$CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OC_2H_5 + NH_2^- \longrightarrow CH_3\overset{O}{\overset{\|}{C}}-\ddot{C}H-\overset{O}{\overset{\|}{C}}OC_2H_5 + NH_3$$

and one molar equivalent of $NaNH_2$ converts bromobenzene to benzyne (cf. Section 21.11B):

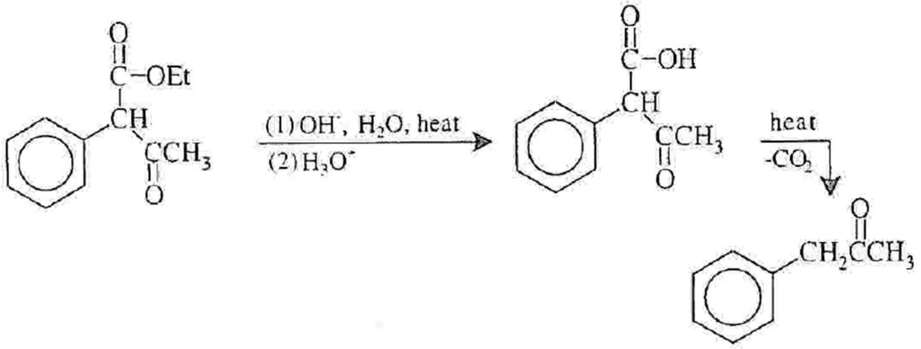


Then the anion of acetoacetic ester adds to the benzyne as it forms in the mixture.

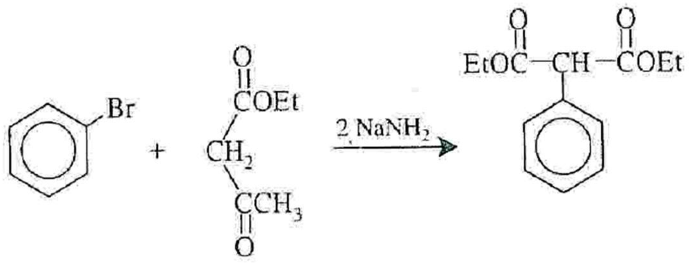


This is the end product of the addition.

(b) 1-phenyl-2-propanone, as follows:

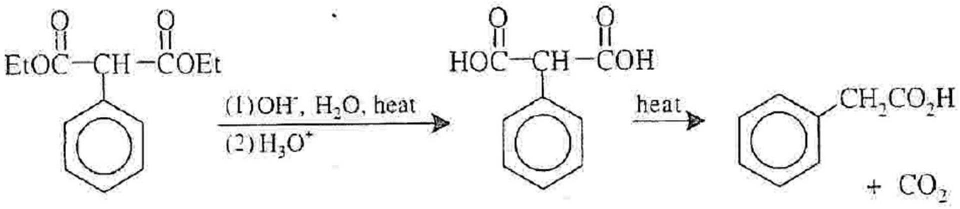


(c) By treating bromobenzene with diethyl malonate and two molar equivalents of $NaNH_2$ to form diethyl phenylmalonate.

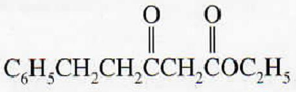


[The mechanism for this reaction is analogous to that given in part (a).]

Then hydrolysis and decarboxylation will convert diethyl phenylmalonate to phenylacetic acid.

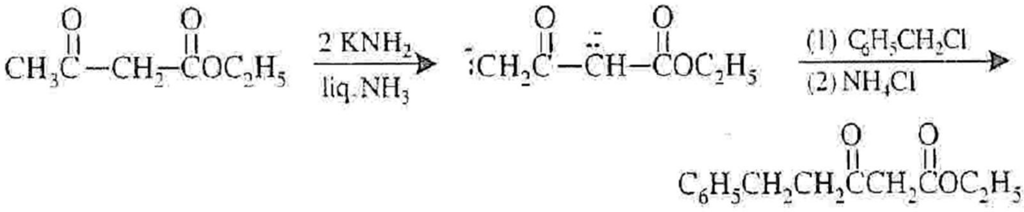


Problem 19.15 ➤ Aşağıda verilen bileşiğin sentezi için etilasetoasetatı nasıl kullanabileceğinizi gösteriniz.



$$C_6H_5CH_2CH_2\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OC_2H_5$$

19.15 Here we alkylate the dianion,

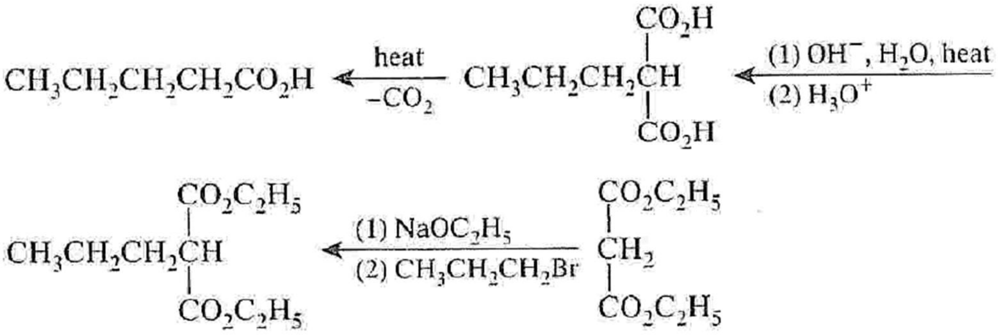


$$CH_3\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}OC_2H_5 \xrightarrow[\text{liq. }NH_3]{2\ KNH_2} {:}\overline{C}H_2\overset{O}{\overset{\|}{C}}-\overset{..}{\overline{C}}H-\overset{O}{\overset{\|}{C}}OC_2H_5 \xrightarrow[(2)\ NH_4Cl]{(1)\ C_6H_5CH_2Cl} C_6H_5CH_2CH_2\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OC_2H_5$$

Problem 19.16 ➤ Aşağıdaki her bir bileşiğin malonik ester sentezindeki bütün basamakları gösteriniz. (a) Pentanoik asit, (b) 2-metilpentanoik asit, ve (c) 4-metilpentanoik asit.

19.16 Working backward,

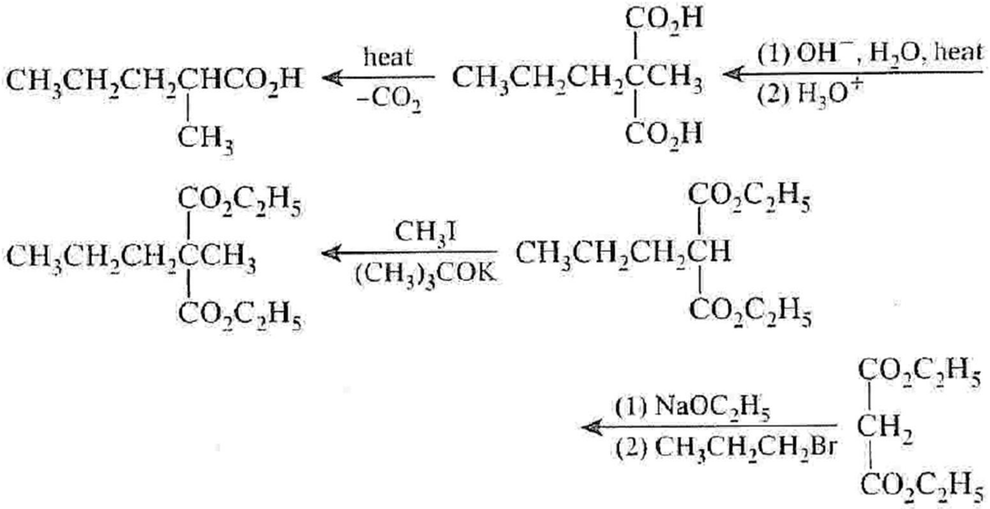
(a)



$$CH_3CH_2CH_2CH_2CO_2H \xleftarrow[-CO_2]{\text{heat}} CH_3CH_2CH_2CH(CO_2H)_2 \xleftarrow[(2)\ H_3O^+]{(1)\ OH^-,\ H_2O,\ \text{heat}}$$

$$CH_3CH_2CH_2CH(CO_2C_2H_5)_2 \xleftarrow[(2)\ CH_3CH_2CH_2Br]{(1)\ NaOC_2H_5} CH_2(CO_2C_2H_5)_2$$

(b)

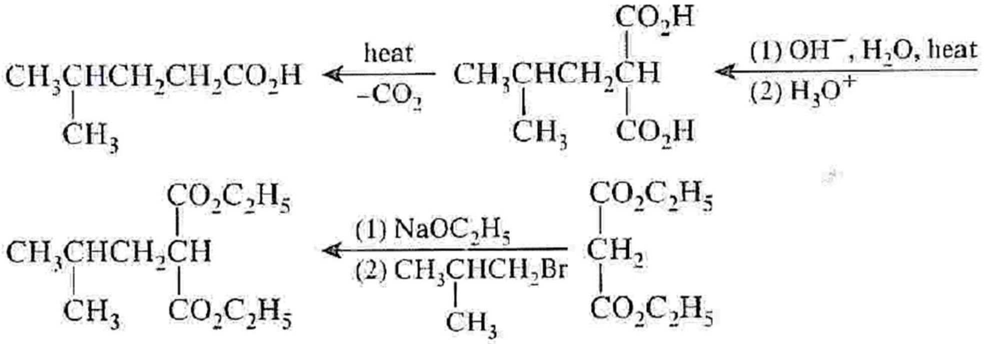


$$CH_3CH_2CH_2\underset{CH_3}{\underset{|}{C}}HCO_2H \xleftarrow[-CO_2]{\text{heat}} CH_3CH_2CH_2C(CH_3)(CO_2H)_2 \xleftarrow[(2)\ H_3O^+]{(1)\ OH^-,\ H_2O,\ \text{heat}}$$

$$CH_3CH_2CH_2C(CH_3)(CO_2C_2H_5)_2 \xleftarrow[(CH_3)_3COK]{CH_3I} CH_3CH_2CH_2CH(CO_2C_2H_5)_2$$

$$\xleftarrow[(2)\ CH_3CH_2CH_2Br]{(1)\ NaOC_2H_5} CH_2(CO_2C_2H_5)_2$$

(c)

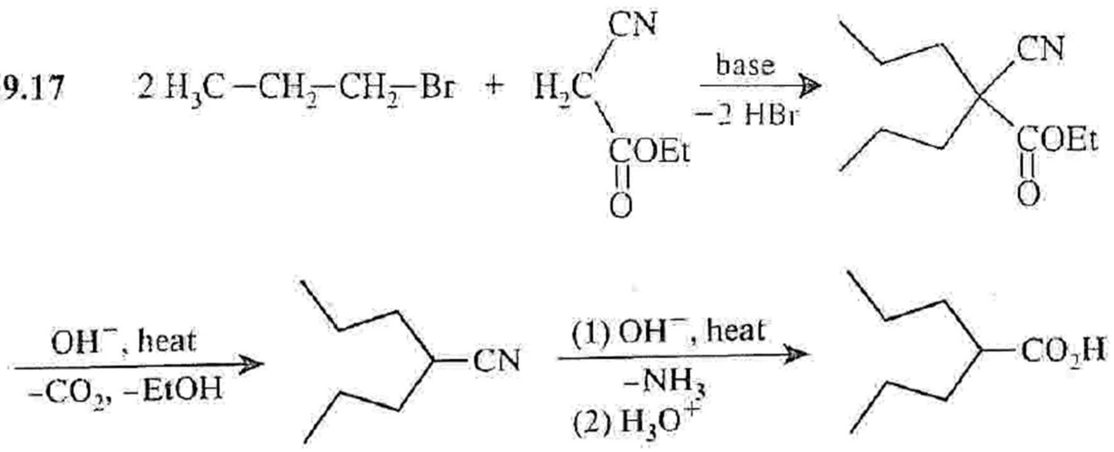


$$CH_3\underset{CH_3}{\underset{|}{C}}HCH_2CH_2CO_2H \xleftarrow[-CO_2]{\text{heat}} CH_3\underset{CH_3}{\underset{|}{C}}HCH_2CH(CO_2H)_2 \xleftarrow[(2)\ H_3O^+]{(1)\ OH^-,\ H_2O,\ \text{heat}}$$

$$CH_3\underset{CH_3}{\underset{|}{C}}HCH_2CH(CO_2C_2H_5)_2 \xleftarrow[(2)\ CH_3\underset{CH_3}{\underset{|}{C}}HCH_2Br]{(1)\ NaOC_2H_5} CH_2(CO_2C_2H_5)_2$$

Antiepileptik ilaç olan valproik asit, 2-propilpentanoik asittir (sodyum tuzu olarak kullanılır). Valproik asitin bir ticari sentezi etilsiyano asetatla başlar. Bu sentezin sondan bir önceki basamağında dekarboksilasyon olur ve son basamakta nitrilin hidrolizi gerçekleşir. Bu sentezi gösteriniz. ◄ **Problem 19.17**

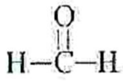
19.17



Valproic acid

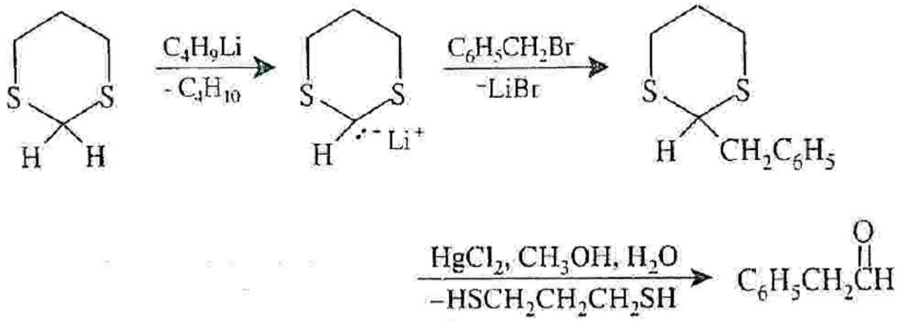
(a) 1,3-Ditiyanın kendisini elde etmek için hangi aldehiti kullanırsınız? (b) Bir 1,3-ditiyanı bir ara ürün gibi kullanarak $C_6H_5CH_2CHO$'yu nasıl sentezlersiniz? (c) Benzaldehiti asetofenona nasıl dönüştürürsünüz? ◄ **Problem 19.18**

19.18 (a) Formaldehyde,

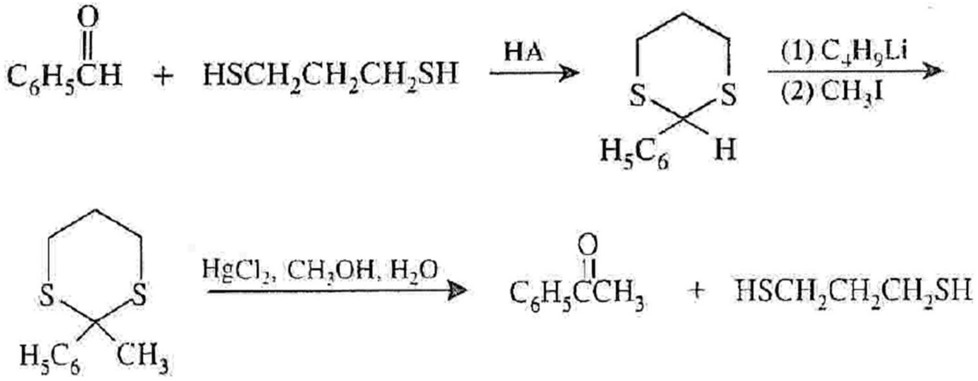


$\text{H}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{H}$

(b)

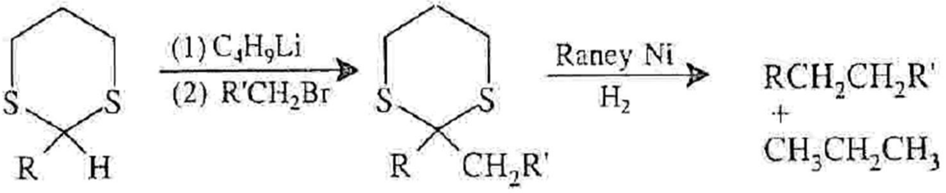


(c)



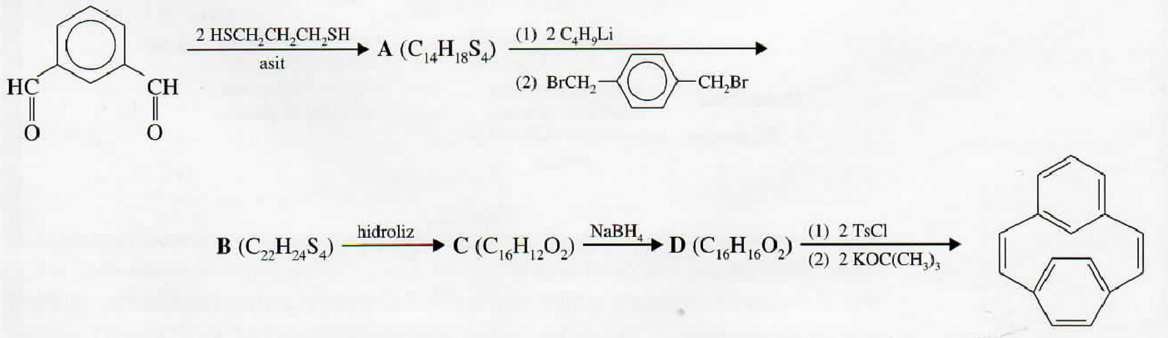
Corey – Seebach yöntemi RCH_2CH_2R' yapısındaki moleküllerin sentezinde de kullanılabilir. Bu nasıl yapılabilir? ◄ **Problem 19.19**

19.19 By treating the thioketal with Raney nickel.



Problem 19.20

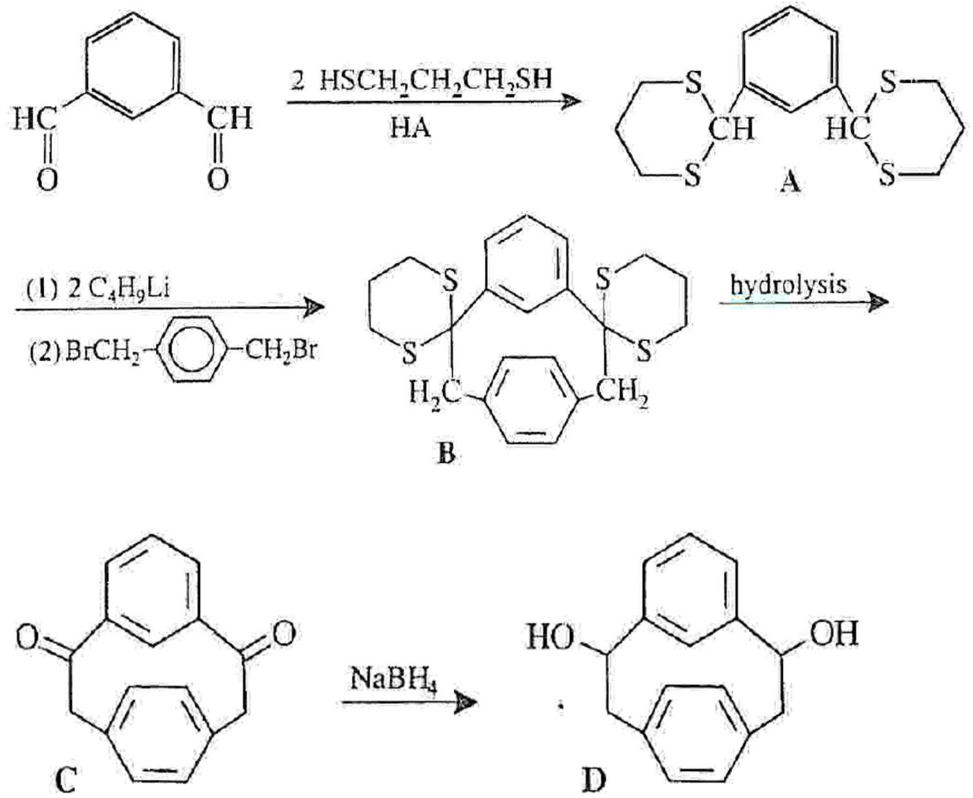
(a) Corey – Seebach yöntemi aşağıda verilen, oldukça gergin yapılı metaparasiklofan olarak adlandırılan bir molekülün eldesinde kullanılmıştır. **A – D** ara ürünlerinin yapıları nedir?



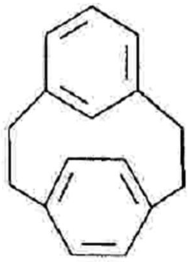
Bir metaparasiklofan

(b) **B** bileşiği aşırı miktarda Raney Ni ile etkileştirildiğinde hangi bileşik elde edilir?

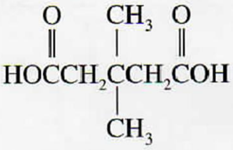
19.20 (a)



(b)



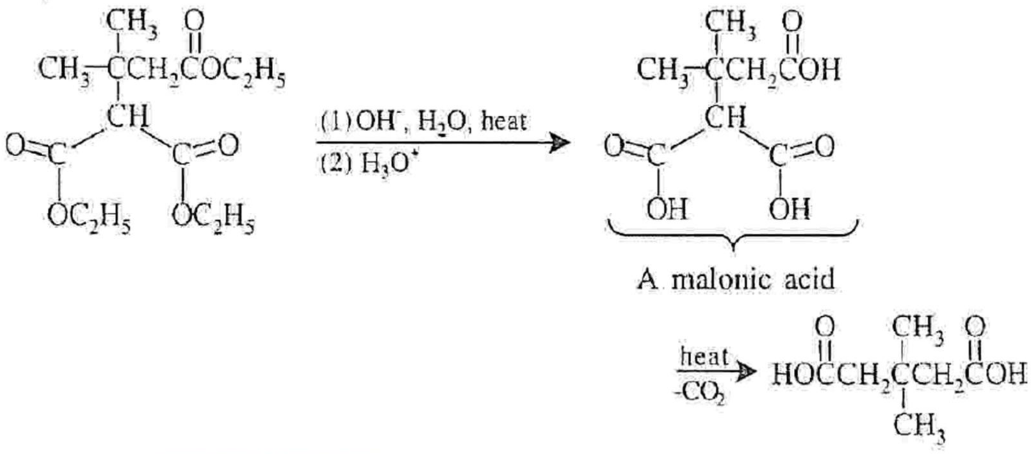
Problem 19.21



$$\mathrm{HO\overset{\displaystyle O}{\overset{\|}{C}}CH_2\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}CH_2\overset{\displaystyle O}{\overset{\|}{C}}OH}$$

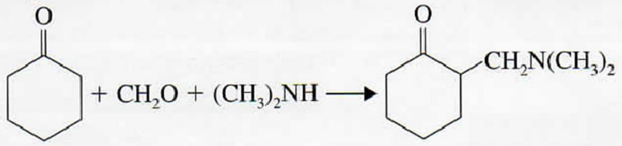
bileşiğini, Michael katılma tepkimesini kullanarak nasıl sentezlersiniz?

19.21

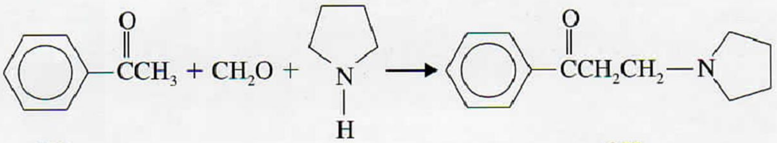


Problem 19.22 ➤ Aşağıdaki Mannich tepkimelerinin ürünlerinin oluşumunu gösteren uygun mekanizmalar yazınız.

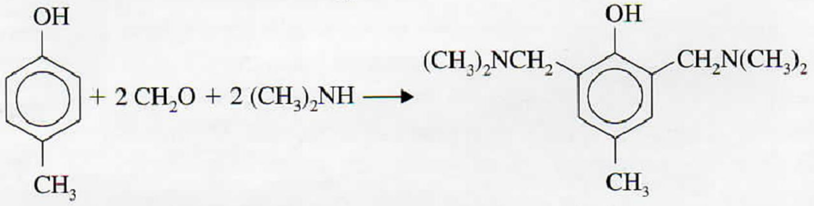
(a)



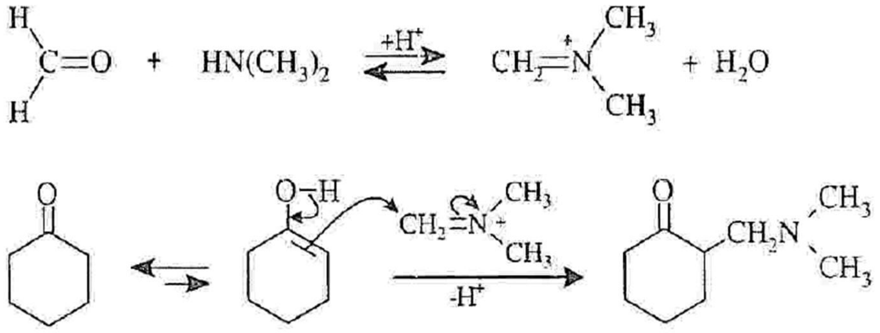
(b)



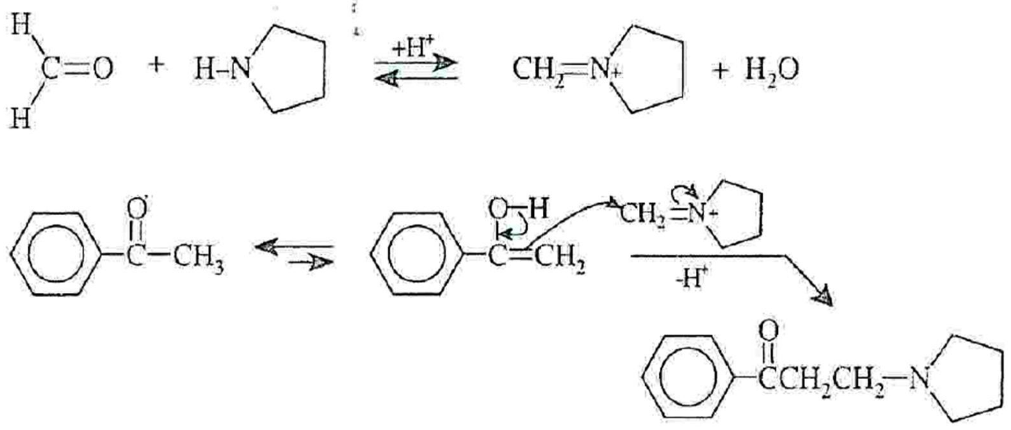
(c)



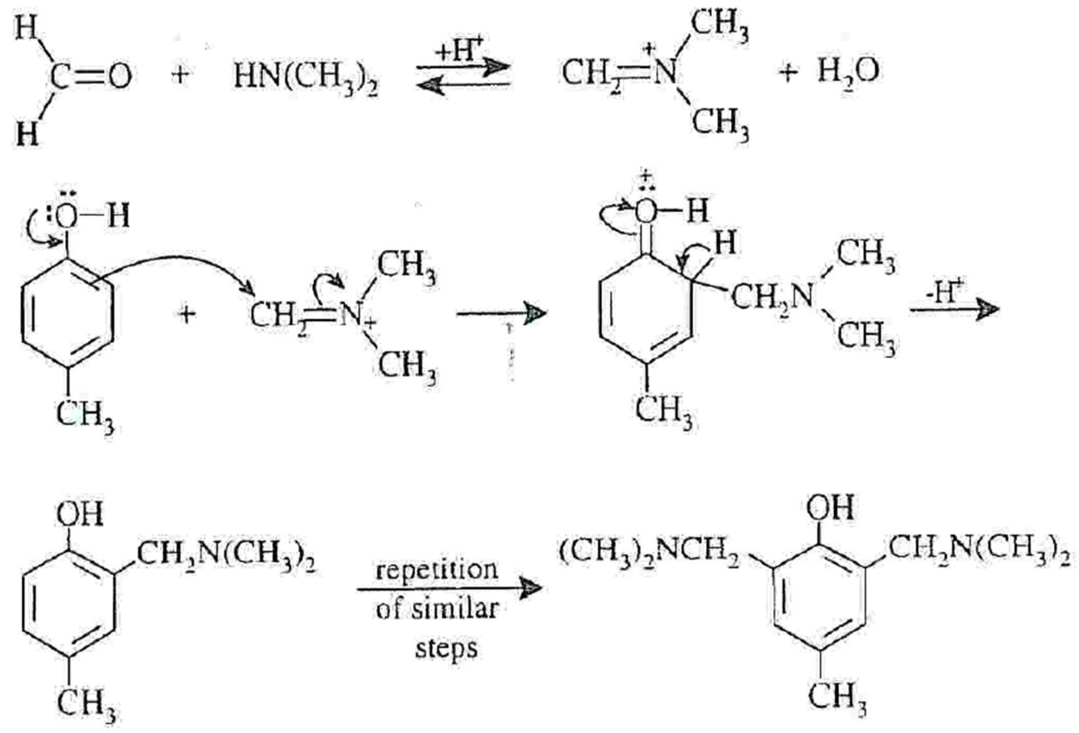
19.22 (a)



(b)



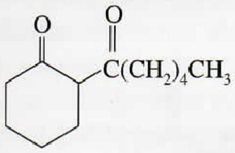
(c)



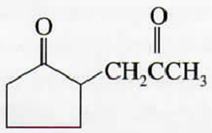
Enaminleri kullanarak aşağıdaki bileşikleri nasıl elde edebileceğinizi gösteriniz:

Problem 19.23

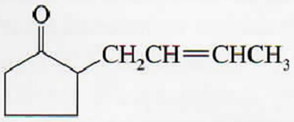
(a)



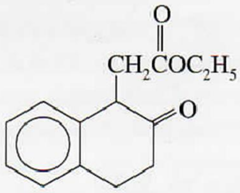
(c)



(b)

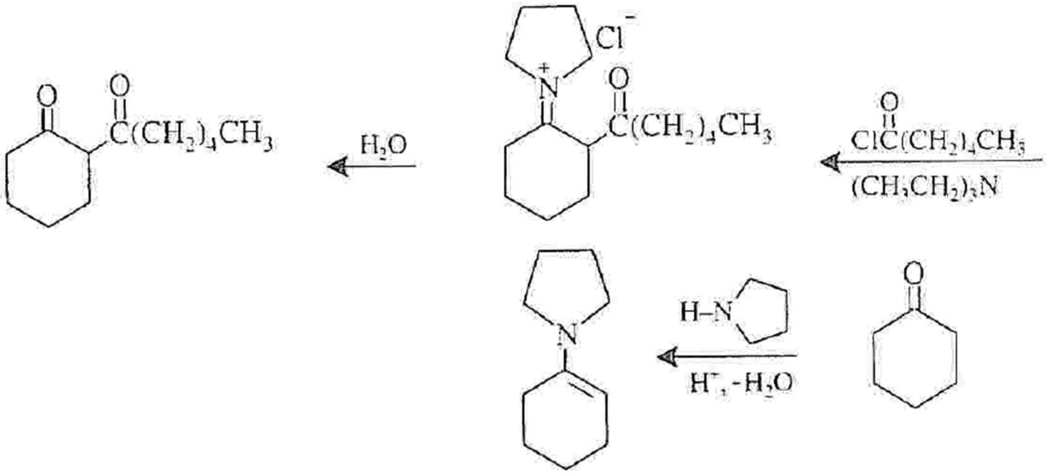


(d)

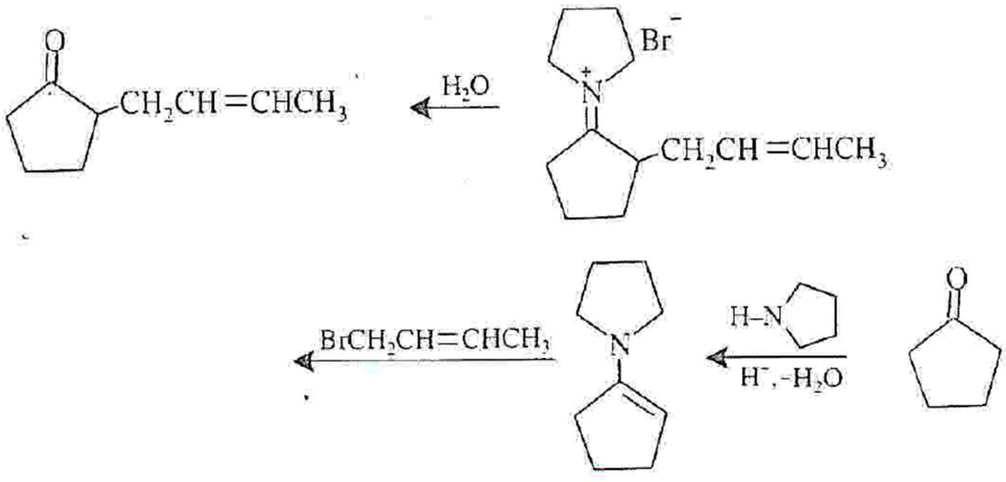


19.23 These syntheses are easier to see if we work backward.

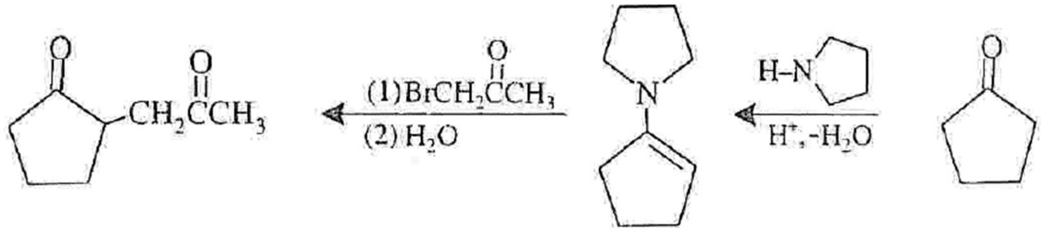
(a)



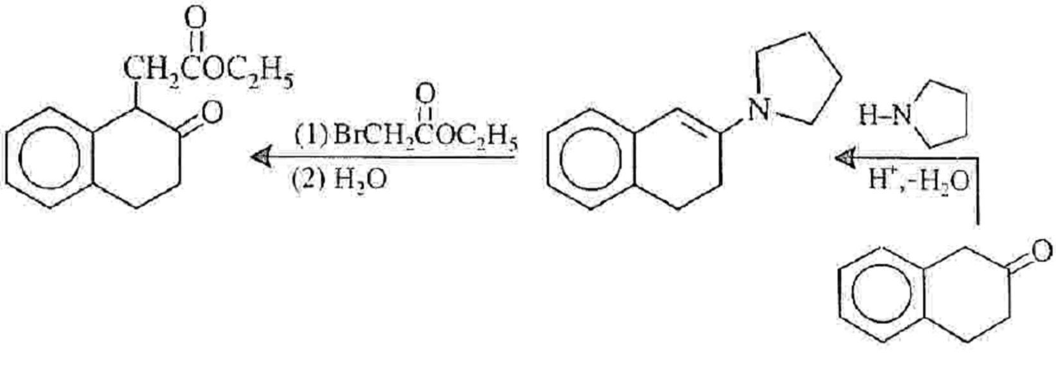
(b)



(c)



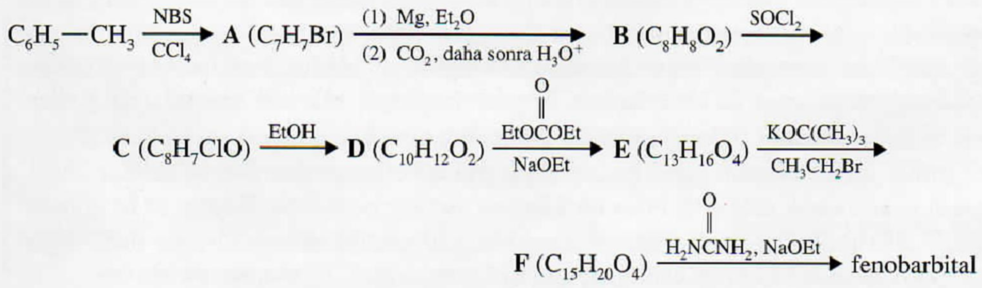
(d)



Fenobarbitalin sentezi aşağıda gösterilmiştir.

Problem 19.24

(a) **A–F** bileşikleri nelerdir? (b) Dietilmalonattan **E**'nin başka bir yolla sentezi için bir yöntem öneriniz.

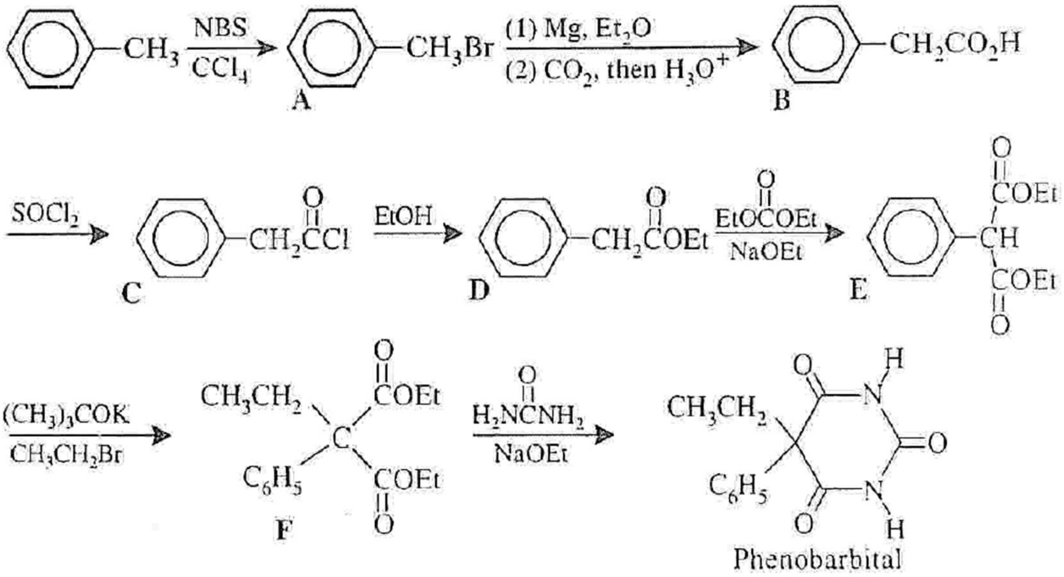


$$C_6H_5{-}CH_3 \xrightarrow[CCl_4]{NBS} \mathbf{A}\ (C_7H_7Br) \xrightarrow[(2)\ CO_2,\ \text{daha sonra}\ H_3O^+]{(1)\ Mg,\ Et_2O} \mathbf{B}\ (C_8H_8O_2) \xrightarrow{SOCl_2}$$

$$\mathbf{C}\ (C_8H_7ClO) \xrightarrow{EtOH} \mathbf{D}\ (C_{10}H_{12}O_2) \xrightarrow[NaOEt]{EtO\overset{O}{\overset{\|}{C}}OEt} \mathbf{E}\ (C_{13}H_{16}O_4) \xrightarrow[CH_3CH_2Br]{KOC(CH_3)_3}$$

$$\mathbf{F}\ (C_{15}H_{20}O_4) \xrightarrow{H_2N\overset{O}{\overset{\|}{C}}NH_2,\ NaOEt} \text{fenobarbital}$$

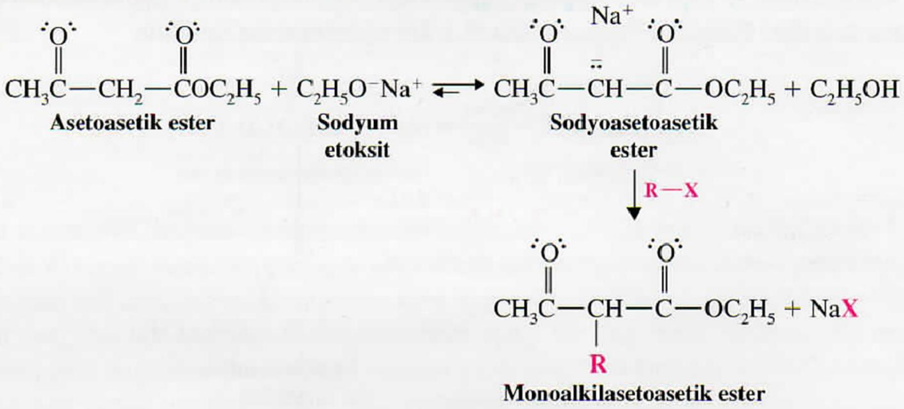
19.24 (a)



(b) See Section 19.3.

19.3 ASETOASETİK ESTER SENTEZİ: METİL KETONLARIN (SÜBSTİTÜE ASETONLAR) SENTEZİ

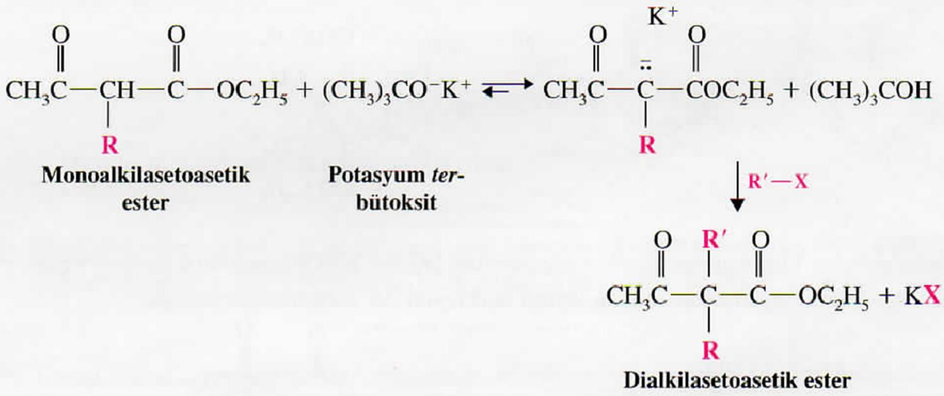
Altbölüm 19.2'de gördüğümüz gibi etil asetoasetatın (asetoasetik ester) metilen protonları etanolün —OH protonlarından daha asidiktir, çünkü, iki karbonil grubu arasında bulunurlar. Bu asitlik, baz olarak sodyum etoksit kullanılarak etil asetoasetatın oldukça kararlı olan enolat anyonuna dönüştürülebileceği anlamına gelir. Daha sonra nükleofilik enolat anyonu bir alkil halojenürle etkileştirilerek alkilleme tepkimesi gerçekleştirilir. Bu sentez **asetoasetik ester sentezi** olarak adlandırılır.



$$CH_3\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}OC_2H_5 + C_2H_5O^-Na^+ \rightleftharpoons CH_3\overset{O}{\overset{\|}{C}}-\overset{..}{C}H-\overset{O}{\overset{\|}{C}}-OC_2H_5 + C_2H_5OH \xrightarrow{R-X} CH_3\overset{O}{\overset{\|}{C}}-\underset{R}{\underset{|}{C}H}-\overset{O}{\overset{\|}{C}}-OC_2H_5 + NaX$$

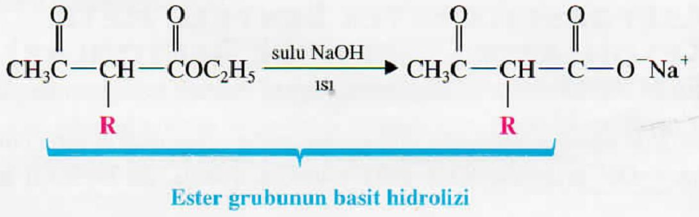
Yukarıdaki tepkimedeki alkilleme bir S_N2 tepkimesi olduğundan en iyi verim, birincil alkil halojenürlerin (birincil allilik ve benzilik halojenürler dahil) veya metil halojenürlerin kullanılmasıyla elde edilir. Tepkime ikincil halojenürlerle yapıldığında verimi düşüktür. Üçüncül halojenürler sadece ayrılma tepkimesi verirler.

Yukarıda gösterilen monoalkillasetoasetik esterin hâlâ oldukça asidik bir hidrojeni vardır. Eğer istenirse ikinci alkilleme yapılabilir. Monoalkilasetoasetik ester asetoasetik esterden daha az asidik (niçin?) olduğu için ikinci alkilleme yapılmak istendiğinde etoksit iyonundan daha kuvvetli baz kullanmak gereklidir. Yaygın olarak potasyum *ter*-bütoksit kullanılır, çünkü sodyum etoksitten daha kuvvetli bazdır. Potasyum *ter*-bütoksitin hacimli bir grup olması nedeniyle transesterleşme tepkimesi meydana gelmez.

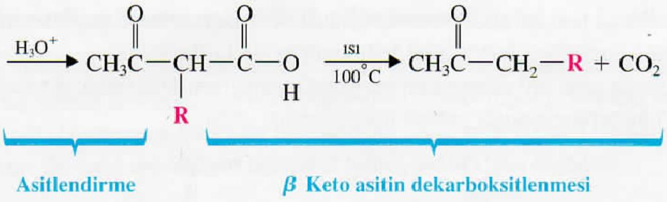


$$CH_3\overset{O}{\overset{\|}{C}}-\underset{R}{\underset{|}{C}H}-\overset{O}{\overset{\|}{C}}-OC_2H_5 + (CH_3)_3CO^-K^+ \rightleftharpoons CH_3\overset{O}{\overset{\|}{C}}-\underset{R}{\underset{|}{\overset{..}{C}}}-\overset{O}{\overset{\|}{C}}OC_2H_5 + (CH_3)_3COH \xrightarrow{R'-X} CH_3\overset{O}{\overset{\|}{C}}-\underset{R}{\underset{|}{\overset{R'}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-OC_2H_5 + KX$$

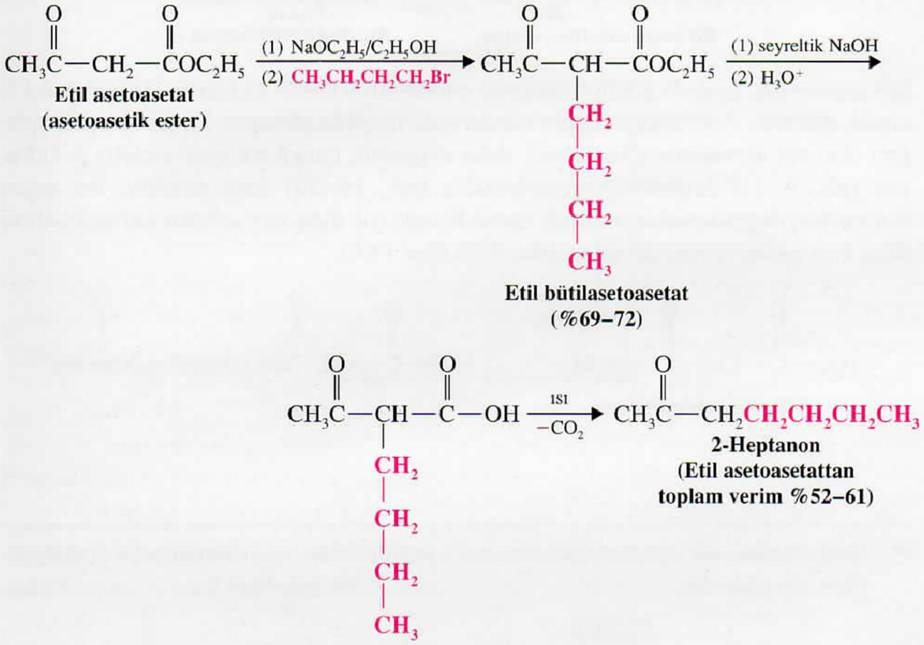
Monosübstitüe metil ketonun (monosübstitüe aseton) sentezinde sadece bir alkilleme yapılır. Daha sonra mono alkil asetoasetik ester sulu sodyum veya potasyum hidroksit kullanılarak hidroliz edilir. Karışımın daha sonra asitlendirilmesiyle bir alkil asetoasetik asit oluşur ve bu β-keto asitin 100°C'a ısıtılmasıyla dekarboksilasyon gerçekleşir (Altbölüm 18.11).



$$\underbrace{CH_3\overset{O}{\overset{\|}{C}}-\underset{R}{\underset{|}{C}H}-\overset{O}{\overset{\|}{C}}OC_2H_5 \xrightarrow[\text{ısı}]{\text{sulu NaOH}} CH_3\overset{O}{\overset{\|}{C}}-\underset{R}{\underset{|}{C}H}-\overset{O}{\overset{\|}{C}}-O^-Na^+}_{\text{Ester grubunun basit hidrolizi}}$$



Aşağıdaki 2-heptanonun sentezi bunun için özel bir örnektir:



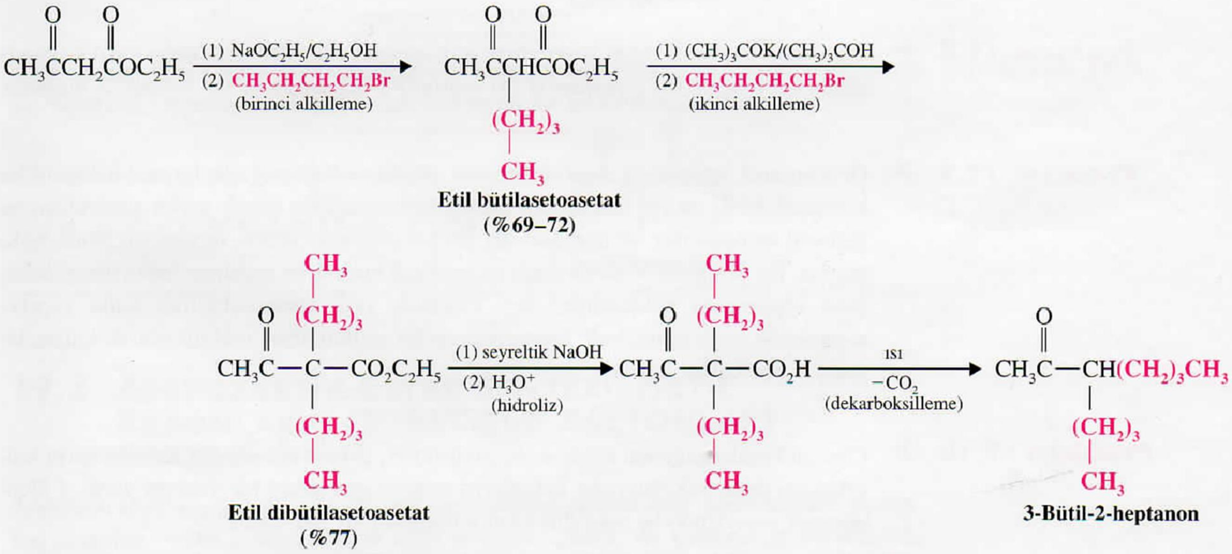
(1) NaOC$_2$H$_5$/C$_2$H$_5$OH
(2) CH$_3$CH$_2$CH$_2$CH$_2$Br
(1) seyreltik NaOH
(2) H$_3$O$^+$
ısı
−CO$_2$

Etil asetoasetat (asetoasetik ester)

Etil bütilasetoasetat (%69–72)

2-Heptanon (Etil asetoasetattan toplam verim %52–61)

Eğer amacımız disübstitüe aseton elde etmekse, birbirini izleyen iki alkillemeden sonra ürünü, dialkilasetoasetik esteri, hidroliz eder daha sonra da oluşan dialkilasetoasetik asiti dekarboksile ederiz. 3-Bütil-2-heptanonun sentezi bu işleme örnek olarak verilebilir.



(1) NaOC$_2$H$_5$/C$_2$H$_5$OH
(2) CH$_3$CH$_2$CH$_2$CH$_2$Br
(birinci alkilleme)
(1) (CH$_3$)$_3$COK/(CH$_3$)$_3$COH
(2) CH$_3$CH$_2$CH$_2$CH$_2$Br
(ikinci alkilleme)
(1) seyreltik NaOH
(2) H$_3$O$^+$
(hidroliz)
ısı
−CO$_2$
(dekarboksilleme)

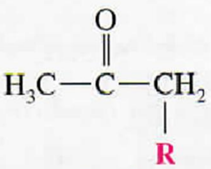
Etil bütilasetoasetat (%69–72)

Etil dibütilasetoasetat (%77)

3-Bütil-2-heptanon

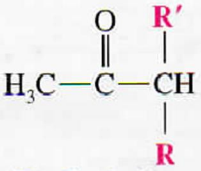
Verilen örnekteki her iki alkillemenin aynı alkil halojenürlerle yapılmış olmasına rağmen sentezde gerekliyse farklı alkil halojenürler de kullanılabilir.

Gördüğümüz gibi, etil asetoasetat aşağıdaki genel formüllü sübstitüe asetonların (metil ketonlar) hazırlanmasında yararlı reaktiflerdir.



$H_3C-\overset{\overset{O}{\|}}{C}-\underset{\underset{R}{|}}{CH_2}$

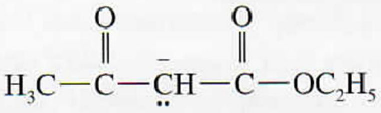
Bir monosübstitüe aseton



$H_3C-\overset{\overset{O}{\|}}{C}-\overset{\overset{R'}{|}}{\underset{\underset{R}{|}}{CH}}$

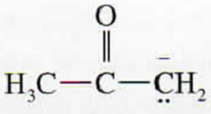
Bir disübstitüe aseton

Etil asetoasetat, aşağıda görülen asetonun enolatının **sentetik eşdeğeri** (Altbölüm 8.17) olarak davranır. Asetonun enolatını oluşturmak mümkün olmasına karşın sentetik eşdeğeri olan etil asetoasetatın kullanımı daha uygundur, çünkü etil asetoasetatın α-hidrojeni (pK_a 9 – 11) asetonun hidrojenlerinden (pK_a 19 – 20) daha asidiktir. Bu anyon (asetondan) doğrudan oluşturulmak istenildiğinde çok daha kuvvetli baz kullanılmalı ve daha özel şartlar uygulanmalıdır (bkz. Altbölüm 19.6).



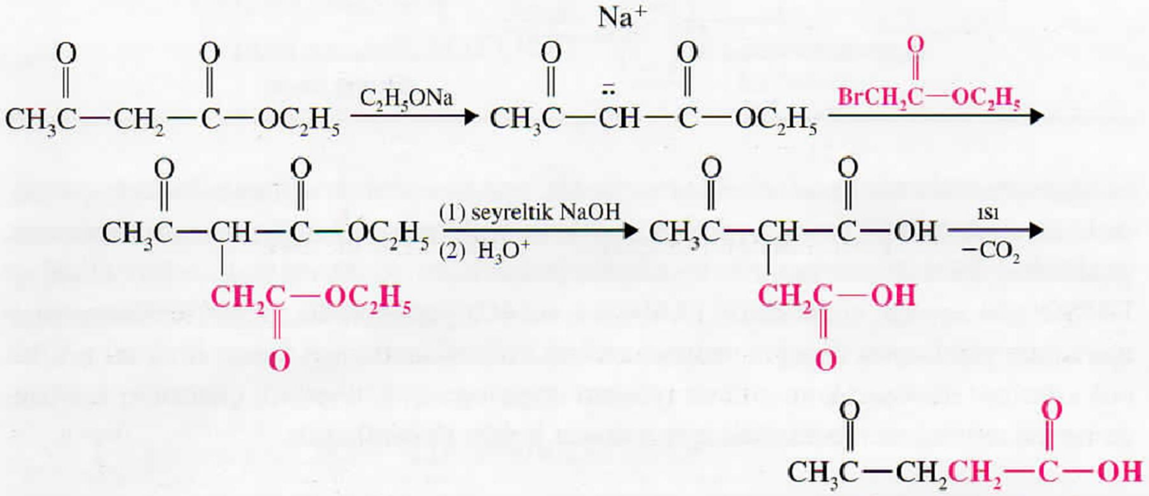
$H_3C-\overset{\overset{O}{\|}}{C}-\underset{..}{\overset{-}{C}H}-\overset{\overset{O}{\|}}{C}-OC_2H_5$

Etil asetoasetat anyonu



$H_3C-\overset{\overset{O}{\|}}{C}-\underset{..}{\overset{-}{C}H_2}$ **'nin sentetik eşdeğeridir**

Asetoasetik ester sentezleri, halo esterler ve haloketonlar kullanılarak da yapılabilir. α-Halo esterlerin kullanılması γ-keto asitlerin eldesinde elverişli bir sentez sağlar.



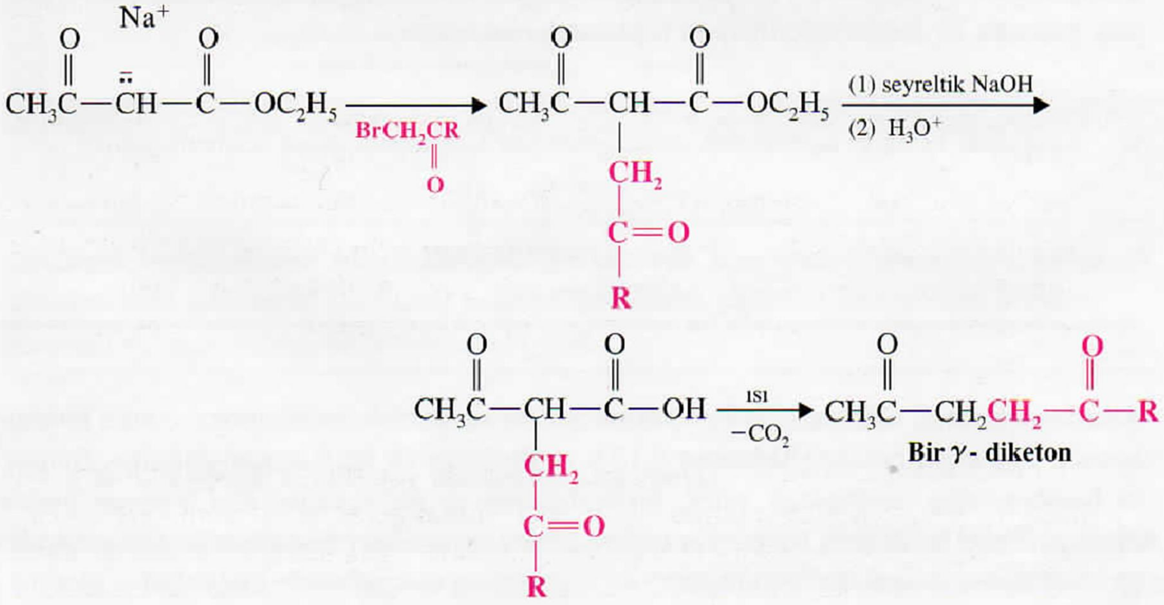
$$CH_3\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5 \xrightarrow{C_2H_5ONa} CH_3\overset{\overset{O}{\|}}{C}-\overset{..}{\bar{C}H}-\overset{\overset{O}{\|}}{C}-OC_2H_5\ Na^+ \xrightarrow{BrCH_2\overset{\overset{O}{\|}}{C}-OC_2H_5}$$

$$CH_3\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_2\underset{\underset{O}{\|}}{C}-OC_2H_5}{|}}{CH}-\overset{\overset{O}{\|}}{C}-OC_2H_5 \xrightarrow[(2)\ H_3O^+]{(1)\ \text{seyreltik NaOH}} CH_3\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_2\underset{\underset{O}{\|}}{C}-OH}{|}}{CH}-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[-CO_2]{\text{ısı}}$$

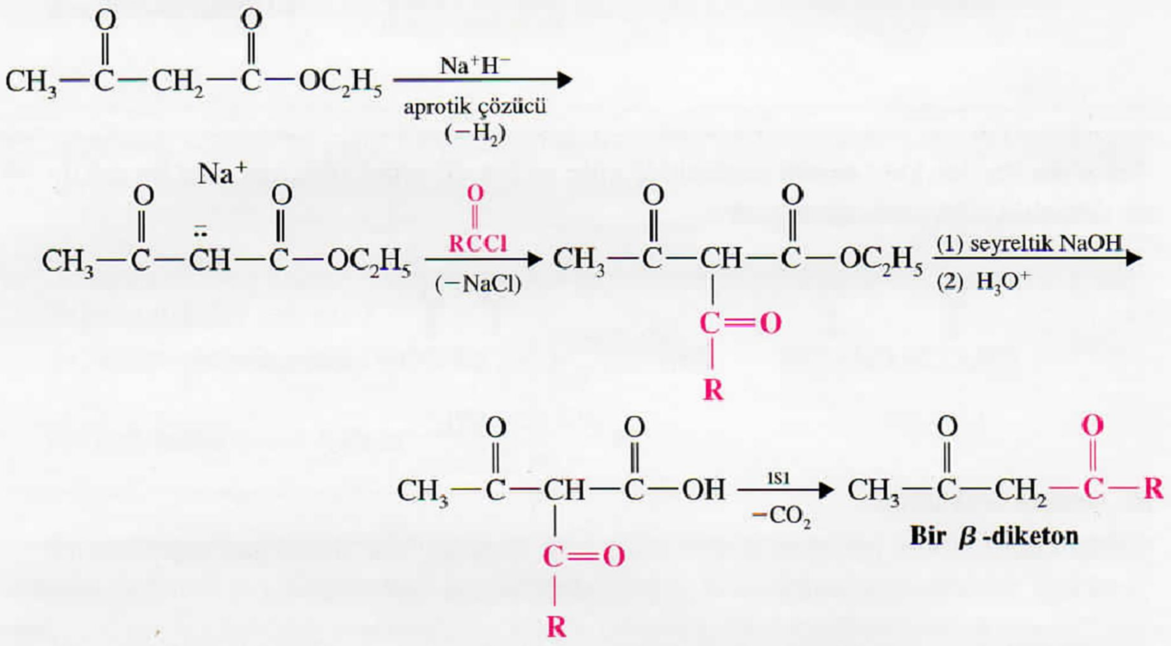
$$CH_3\overset{\overset{O}{\|}}{C}-CH_2CH_2-\overset{\overset{O}{\|}}{C}-OH$$

4-Oksopentanoik asit

Asetoasetik ester sentezinde α-halo ketonların kullanılması γ-diketonların eldesi için genel bir yöntem sağlar:

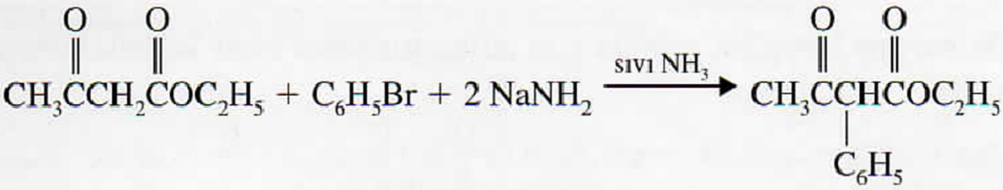


Asetoasetik esterden elde edilen anyonlar, açil klorür veya açil anhidritlerle etkileştirildiklerinde bir açilleme gerçekleşir. Açilleme tepkimeleri etanol içerisinde yapılamaz, çünkü her iki açilleme reaktifi de alkollerle etkileşir. Açilleme tepkimeleri DMF ve DMSO gibi aprotik çözücülerle (Altbölüm 6.14C) yapılmalıdır. (Eğer tepkime etanol içerisinde yapılsaydı, örneğin sodyum etoksit kullanılsaydı, açil klorür hızlı bir şekilde etil esterlere dönüşecek ve etoksit iyonları nötürleşecekti.) Aprotik çözücüler içerisinde enolat anyonunu oluşturmak için sodyum hidrür kullanılabilir.



β-Dikarbonil bileşiklerinin elde edilmesinde Claissen kondensasyonu dışında kullanılabilen başka bir yöntem de asetoasetik esterlerin açillenmesini, bunu izleyen hidroliz ve dekarboksilasyon tepkimelerini içerir.

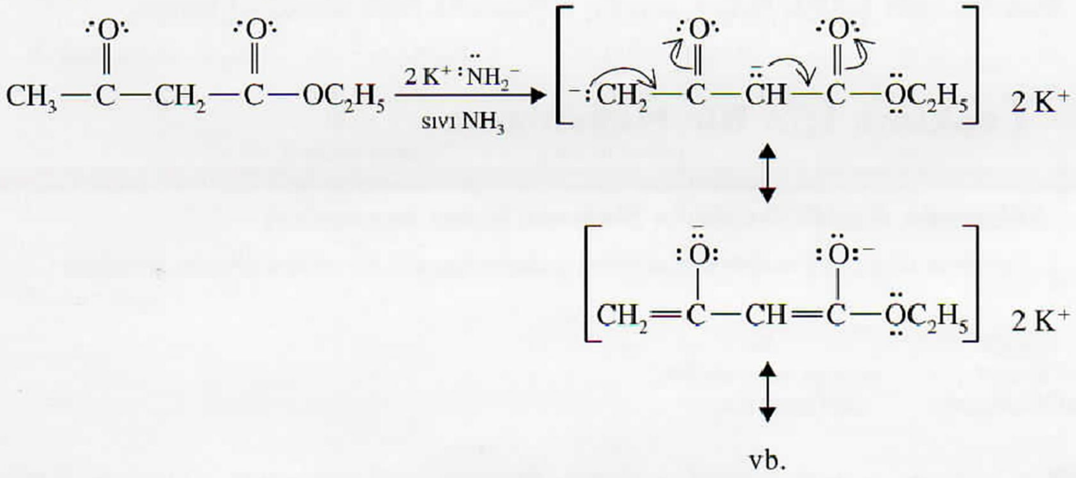
Asetoasetik ester, alkilleme tepkimelerine benzer bir şekilde fenillenmez, çünkü bromobenzen S_N2 tepkimesine [Altbölüm 6.15A ve Problem 19.9(c)] uygun değildir. Bununla beraber, eğer asetoasetik ester, bromobenzen ve *iki eşdeğer mol sodyum amitle* etkileştirilirse fenilleme, bir *benzin mekanizması üzerinden* (Altbölüm 21.11) gerçekleşir. Net tepkime aşağıda verilmiştir:



$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OC_2H_5} + \mathrm{C_6H_5Br} + 2\,\mathrm{NaNH_2} \xrightarrow{\text{sıvı NH}_3} \mathrm{CH_3\overset{O}{\overset{\|}{C}}\underset{\underset{C_6H_5}{|}}{C}H\overset{O}{\overset{\|}{C}}OC_2H_5}$$

Malonik esterler $\left(\mathrm{RO\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OR}\right)$ de benzer yöntemlerle fenillenebilirler.

Asetoasetik ester sentezinin diğer bir şekli, sıvı amonyak içerisinde potasyum amit gibi çok kuvvetli bir baz kullanılarak bir asetoasetik esterin rezonans kararlı *dianyonuna* dönüştürülmesini içerir.



$$\mathrm{CH_3-\overset{:\ddot{O}:}{\overset{\|}{C}}-CH_2-\overset{:\ddot{O}:}{\overset{\|}{C}}-OC_2H_5} \xrightarrow[\text{sıvı NH}_3]{2\,K^+\,:\ddot{N}H_2^-} \left[{}^-:\mathrm{CH_2-\overset{:\ddot{O}:}{\overset{\|}{C}}-\overset{-}{\ddot{C}}H-\overset{:\ddot{O}:}{\overset{\|}{C}}-\ddot{O}C_2H_5}\right]\ 2\,K^+$$

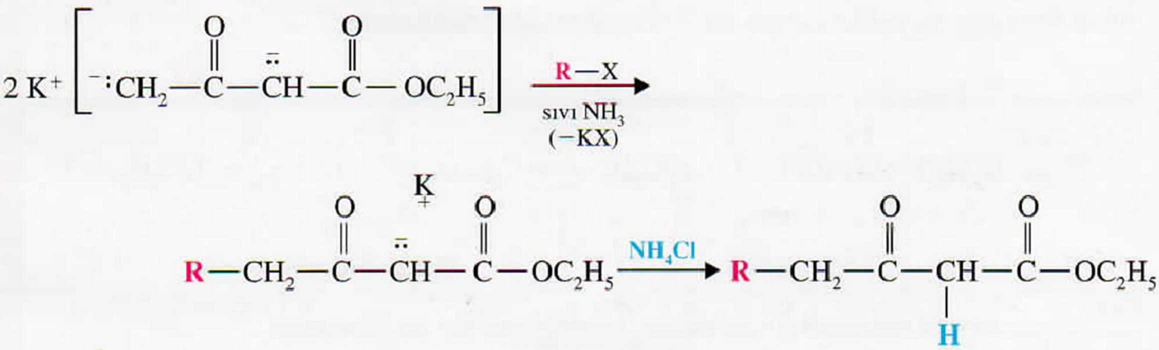
$$\updownarrow$$

$$\left[\mathrm{CH_2=\overset{:\ddot{O}:^-}{\overset{|}{C}}-CH=\overset{:\ddot{O}:^-}{\overset{|}{C}}-\ddot{O}C_2H_5}\right]\ 2\,K^+$$

$$\updownarrow$$

vb.

Bu dianyon, bir mol birincil (veya metil) halojenürle etkileştirildiğinde iç tarafta bulunan karbondan daha çok uçta bulunan karbonda alkillenme gerçekleşir. Bu alkilleme tepkimesinin bu şekilde yönlenmesi, uçtaki karbonyonun daha kuvvetli bazik (ve dolayısıyla daha fazla nükleofilik) özellik göstermesinden kaynaklanır. Bu karbanyon daha baziktir, çünkü sadece bitişik bir karbonil grubu tarafından kararlı kılınır. Monoalkilleme meydana geldikten sonra anyon, amonyum klorür ilavesiyle protonlanabilir.

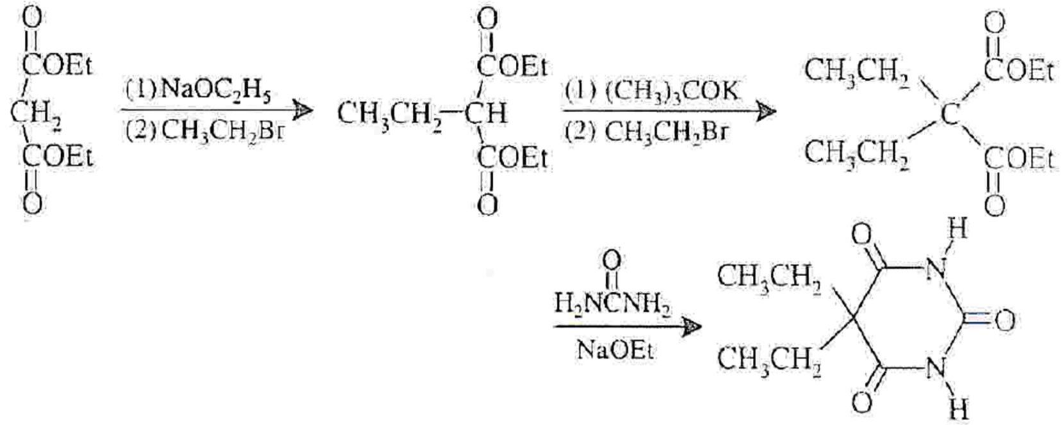


$$2\,K^+\left[{}^-:\mathrm{CH_2-\overset{O}{\overset{\|}{C}}-\overset{..}{\underset{-}{C}}H-\overset{O}{\overset{\|}{C}}-OC_2H_5}\right] \xrightarrow[\substack{\text{sıvı NH}_3\\(-\mathrm{KX})}]{\mathrm{R-X}}$$

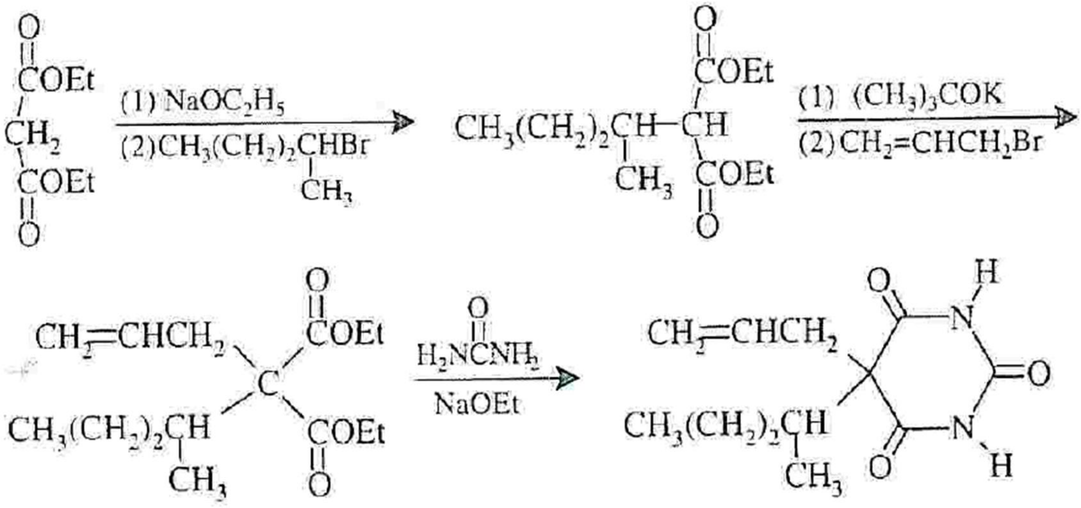
$$\mathrm{R-CH_2-\overset{O}{\overset{\|}{C}}-\overset{\overset{K}{+}}{\overset{..}{\underset{-}{C}}H}-\overset{O}{\overset{\|}{C}}-OC_2H_5} \xrightarrow{\mathrm{NH_4Cl}} \mathrm{R-CH_2-\overset{O}{\overset{\|}{C}}-\underset{\underset{H}{|}}{C}H-\overset{O}{\overset{\|}{C}}-OC_2H_5}$$

Dietil malonat ile üreden başlayarak ve diğer gerekli reaktifleri kullanarak veronal ve sekonal sentezini tasarlayınız. ◄ **Problem 19.25**

19.25

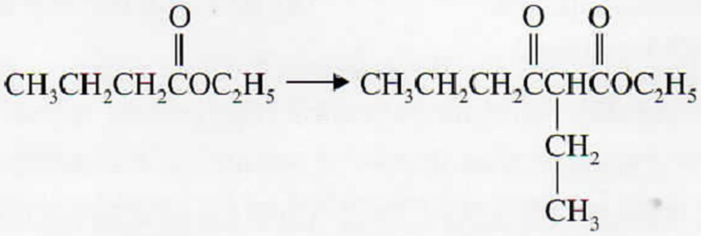


Veronal



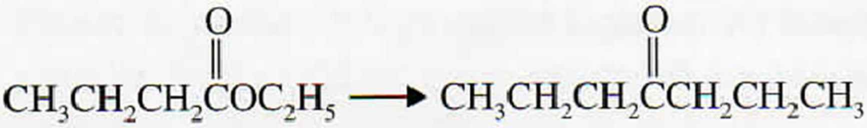
Seconal

19.26 Verilen bileşiklerden başlayarak ve gerekli olan diğer reaktifleri kullanarak aşağıda sentezlerin bütün basamaklarını gösteriniz. Bir önceki basamakta yazdığınız basamakları sonraki problemde tekrarlamayınız, kaldığınız yerden diğer basamağı tamamlayınız.

(a) 

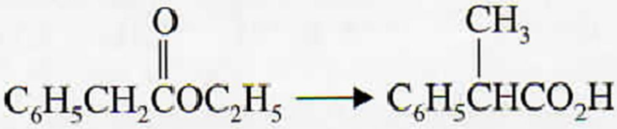
$$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}OC_2H_5 \longrightarrow CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}\underset{\underset{CH_3}{|}}{\underset{CH_2}{\underset{|}{C}}}H\overset{O}{\overset{\|}{C}}OC_2H_5$$

(b)



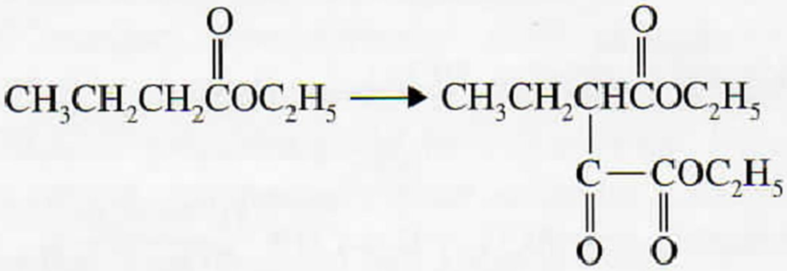
$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}OC_2H_5 \longrightarrow CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_2CH_2CH_3$

(c)



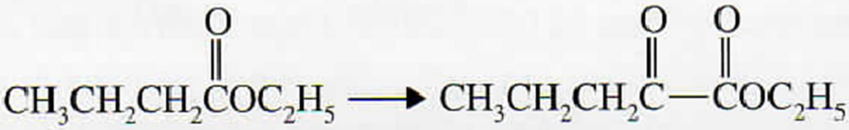
$C_6H_5CH_2\overset{\overset{O}{\|}}{C}OC_2H_5 \longrightarrow C_6H_5\overset{\overset{CH_3}{|}}{C}HCO_2H$

(d)



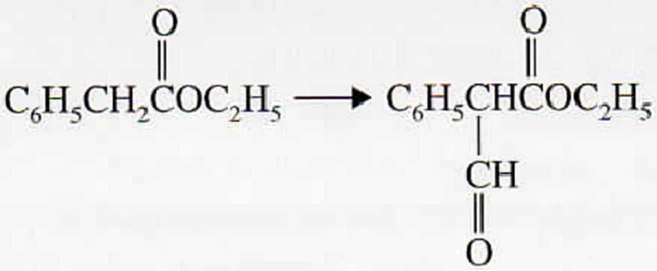
$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}OC_2H_5 \longrightarrow CH_3CH_2\underset{\underset{\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}OC_2H_5}{|}}{}}{C}H\overset{\overset{O}{\|}}{C}OC_2H_5$

(e)



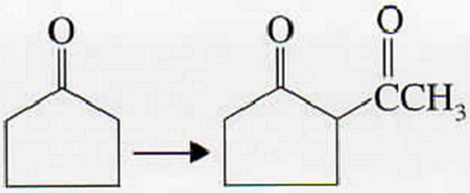
$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}OC_2H_5 \longrightarrow CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}OC_2H_5$

(f)

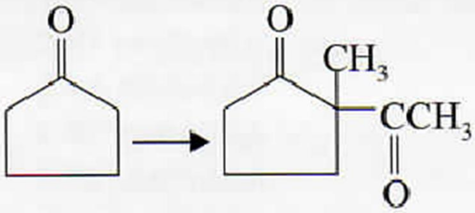


$C_6H_5CH_2\overset{\overset{O}{\|}}{C}OC_2H_5 \longrightarrow C_6H_5\underset{\underset{\underset{\underset{O}{\|}}{CH}}{|}}{C}H\overset{\overset{O}{\|}}{C}OC_2H_5$

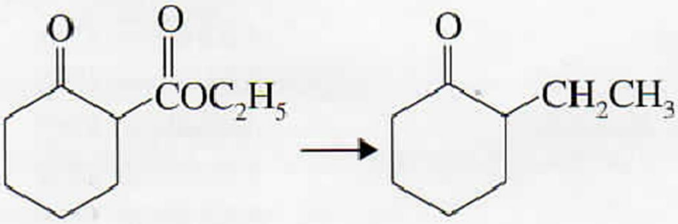
(g)



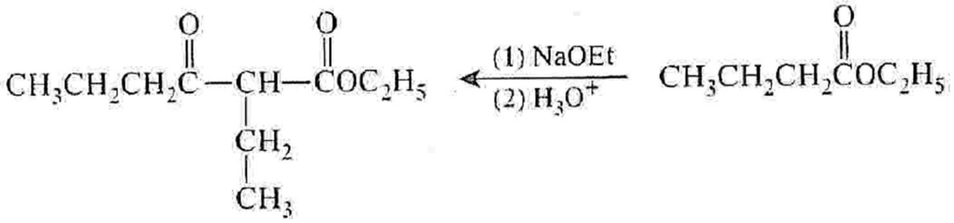
(h)



(i)

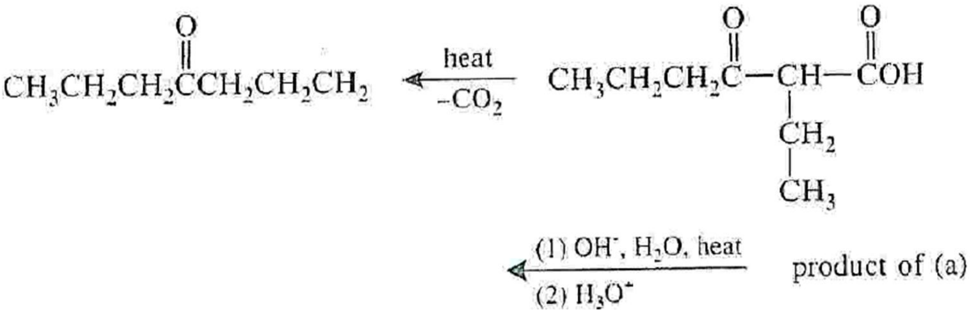


19.26 (a)



$$\mathrm{CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}-\underset{\begin{subarray}{c}|\\ CH_2\\ |\\ CH_3\end{subarray}}{CH}-\overset{O}{\overset{\|}{C}}OC_2H_5} \xleftarrow[\text{(2) } H_3O^+]{\text{(1) NaOEt}} \mathrm{CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}OC_2H_5}$$

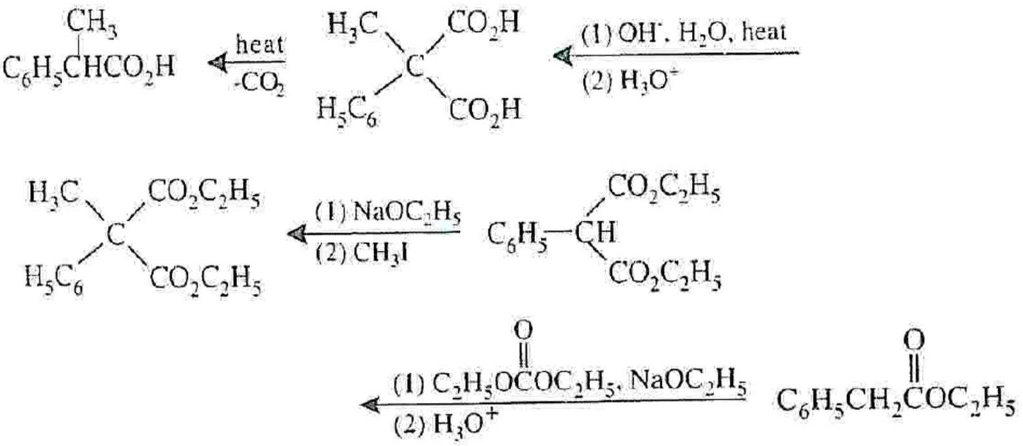
(b)



$$\mathrm{CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2} \xleftarrow[-CO_2]{\text{heat}} \mathrm{CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}-\underset{\begin{subarray}{c}|\\ CH_2\\ |\\ CH_3\end{subarray}}{CH}-\overset{O}{\overset{\|}{C}}OH}$$

$$\xleftarrow[\text{(2) } H_3O^+]{\text{(1) } OH^-,\ H_2O,\ \text{heat}} \text{product of (a)}$$

(c)

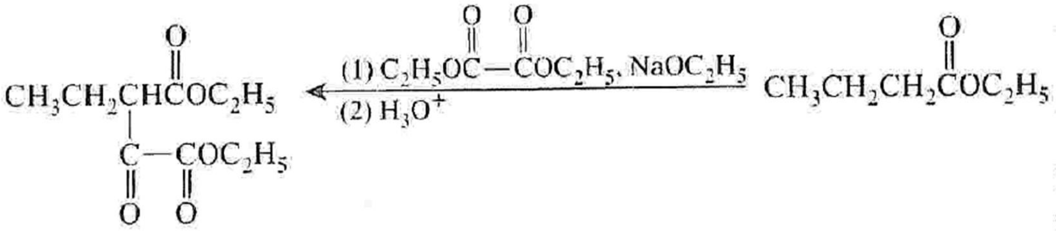


$$\mathrm{C_6H_5\overset{\begin{subarray}{c}CH_3\\ |\end{subarray}}{C}HCO_2H} \xleftarrow[-CO_2]{\text{heat}} \mathrm{(H_3C)(H_5C_6)C(CO_2H)_2} \xleftarrow[\text{(2) } H_3O^+]{\text{(1) } OH^-,\ H_2O,\ \text{heat}}$$

$$\mathrm{(H_3C)(H_5C_6)C(CO_2C_2H_5)_2} \xleftarrow[\text{(2) } CH_3I]{\text{(1) } NaOC_2H_5} \mathrm{C_6H_5-CH(CO_2C_2H_5)_2}$$

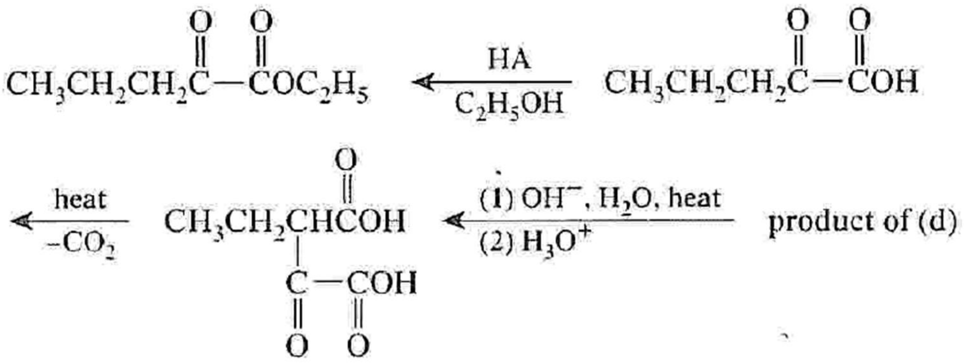
$$\xleftarrow[\text{(2) } H_3O^+]{\text{(1) } C_2H_5O\overset{O}{\overset{\|}{C}}OC_2H_5,\ NaOC_2H_5} \mathrm{C_6H_5CH_2\overset{O}{\overset{\|}{C}}OC_2H_5}$$

(d)

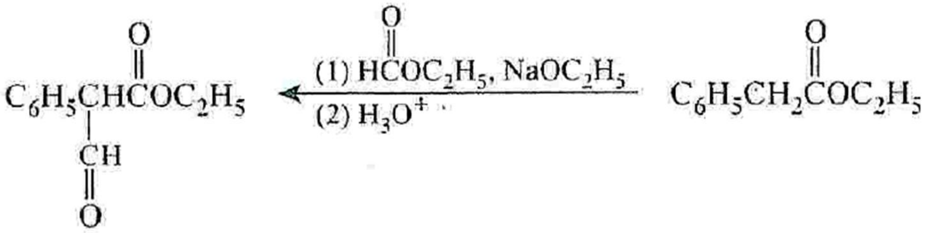


$$\mathrm{CH_3CH_2\underset{\begin{subarray}{c}|\\ \underset{\|}{C}-\underset{\|}{C}OC_2H_5\\ O\quad\ O\end{subarray}}{C}H\overset{O}{\overset{\|}{C}}OC_2H_5} \xleftarrow[\text{(2) } H_3O^+]{\text{(1) } C_2H_5O\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}OC_2H_5,\ NaOC_2H_5} \mathrm{CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}OC_2H_5}$$

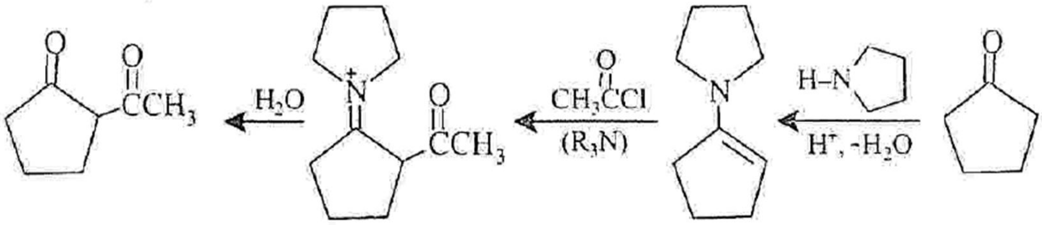
(e)



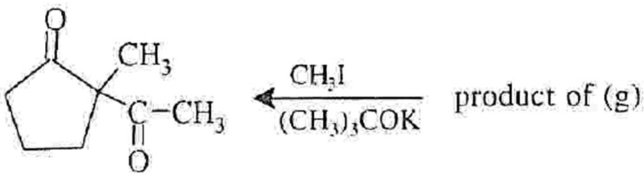
(f)



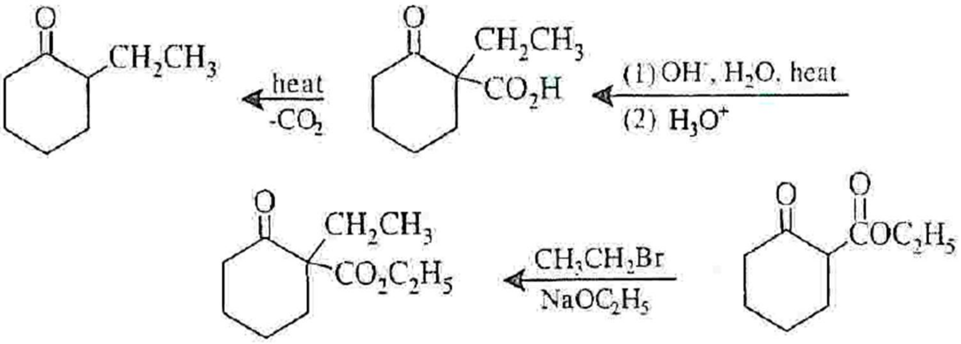
(g)



(h)



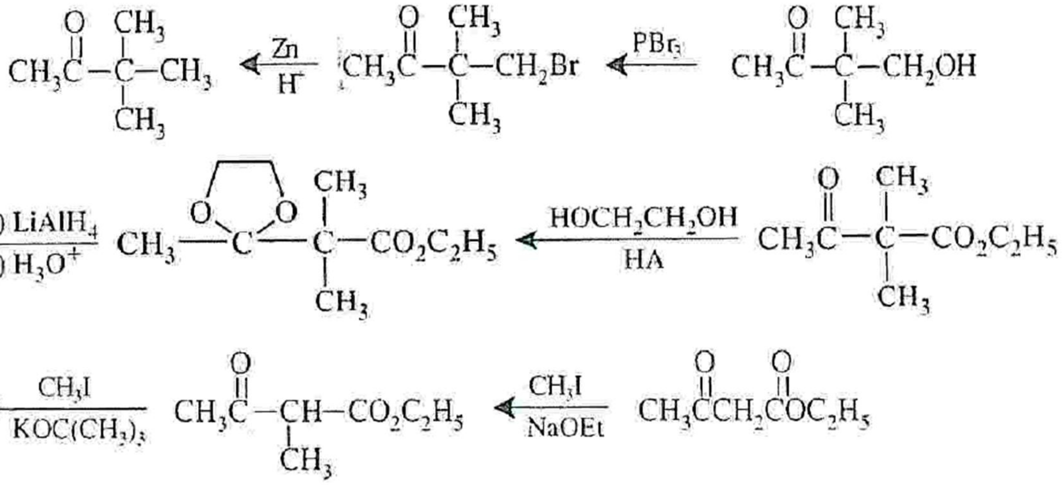
(i)



19.27 Asetoasetik ester ve gerekli olan diğer reaktiflerden başlayarak aşağıdaki bileşikleri sentezleyiniz.

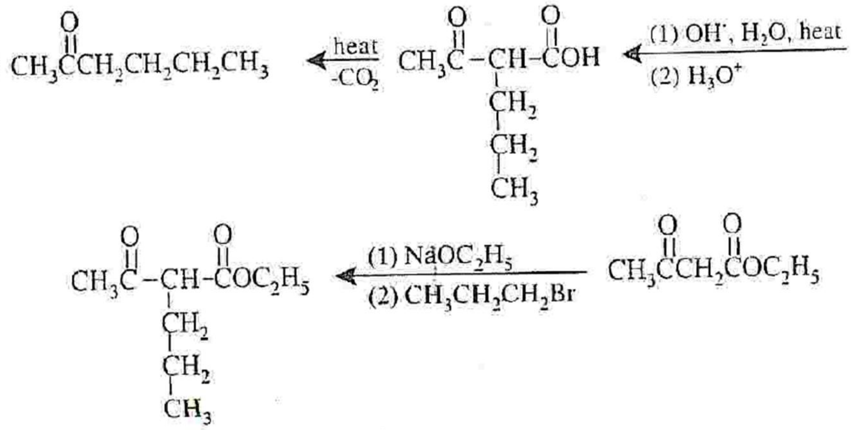
- **(a)** *ter*-Bütil metil keton
- **(b)** 2-Heksanon
- **(c)** 2,5-Heksandion
- **(d)** 4-Hidroksipentanoik asit
- **(e)** 2-Etil-1,3-bütandiol
- **(f)** 1-Fenil-1,3-bütandiol

19.27 (a)

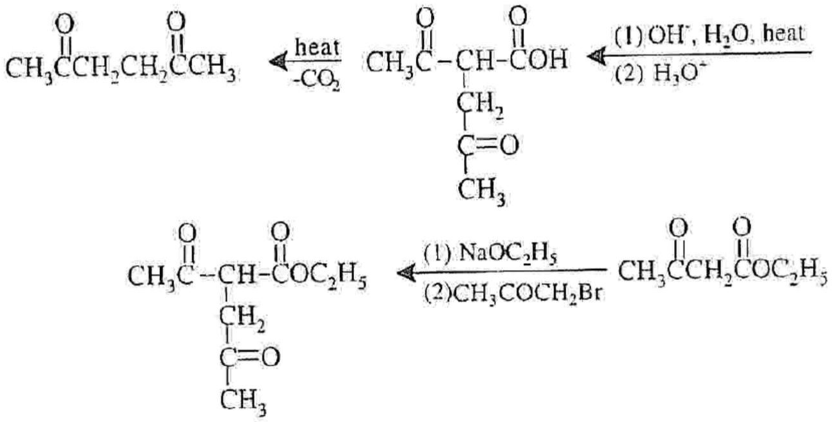


Zn
H⁺
PBr₃
(1) LiAlH₄
(2) H₃O⁺
HOCH₂CH₂OH
HA
CH₃I
KOC(CH₃)₃
CH₃I
NaOEt
CH₃CCH₂COC₂H₅
CH₃C–CH–CO₂C₂H₅
CH₃C–C–CO₂C₂H₅
CH₃C–C–CH₂OH
CH₃C–C–CH₂Br
CH₃C–C–CH₃

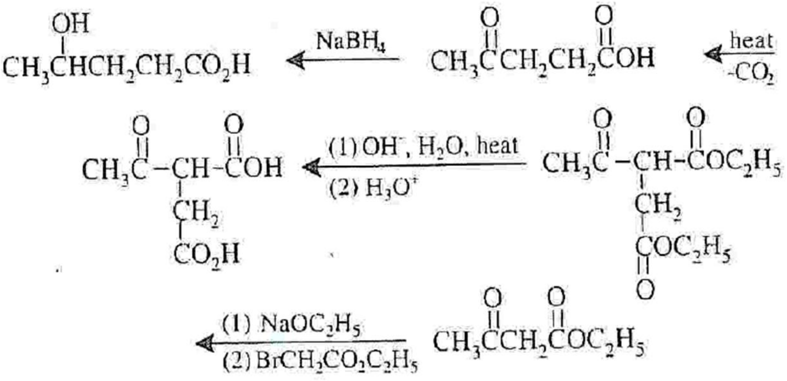
(b)



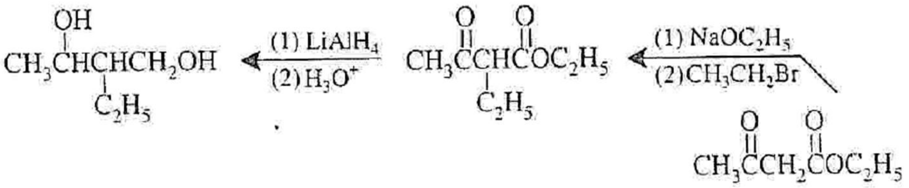
(c)



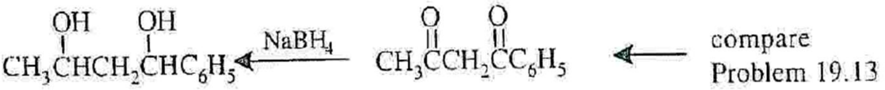
(d)



(e)



(f)



19.28 Aşağıdaki bileşiklerin her birini dietil malonat ve diğer gerekli maddeleri kullanarak sentezleyiniz.

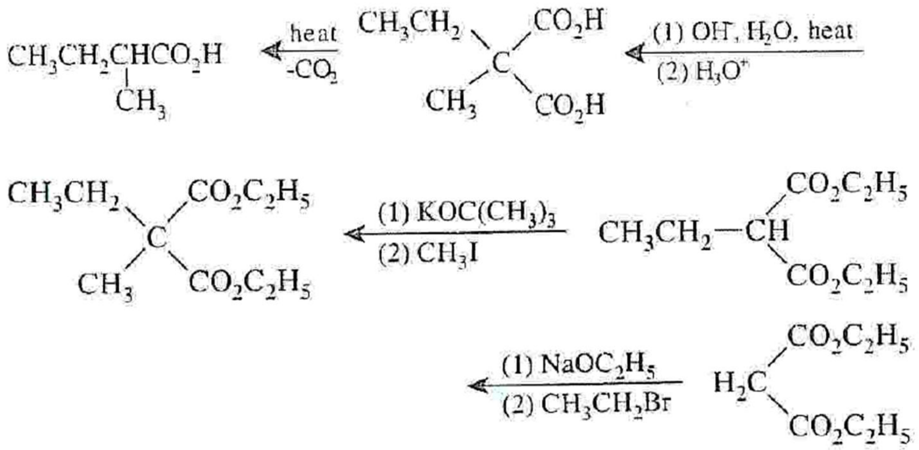
(a) 2-Metilbütanoik asit

(b) 4-Metil-1-pentanol

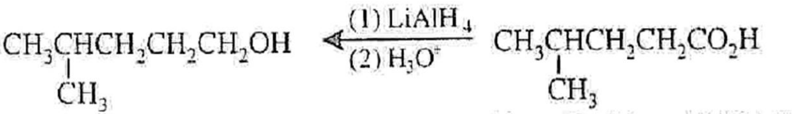
(c) $CH_3CH_2\underset{\displaystyle CH_2OH}{\underset{|}{C}}HCH_2OH$

(d) $HOCH_2CH_2CH_2CH_2OH$

19.28 (a)

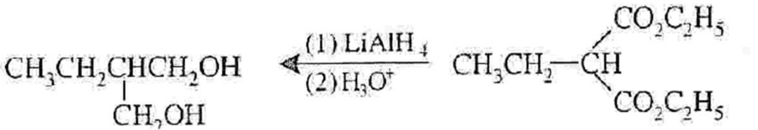


(b)



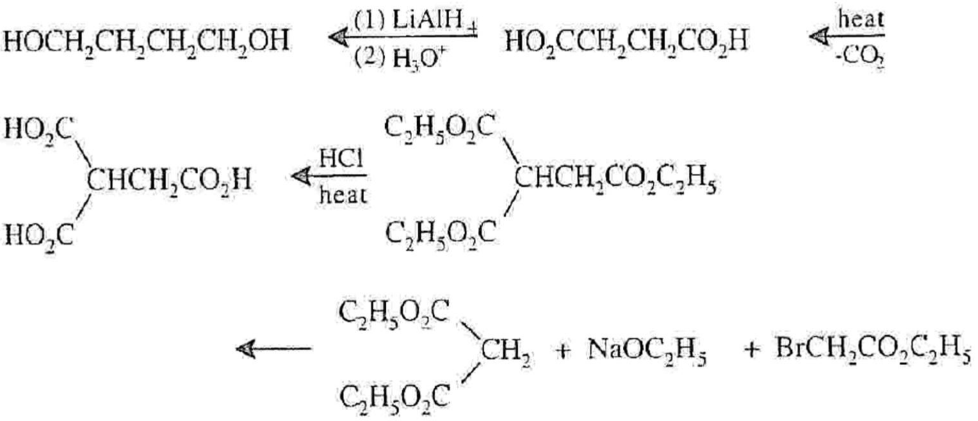
[from Problem 19.16(c)]

(c)

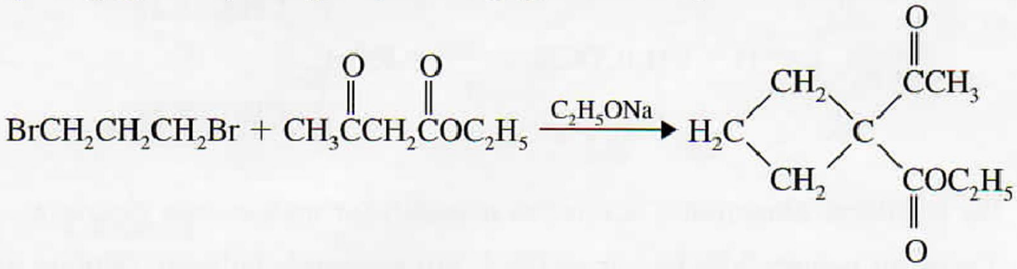


[from (a) above]

(d)

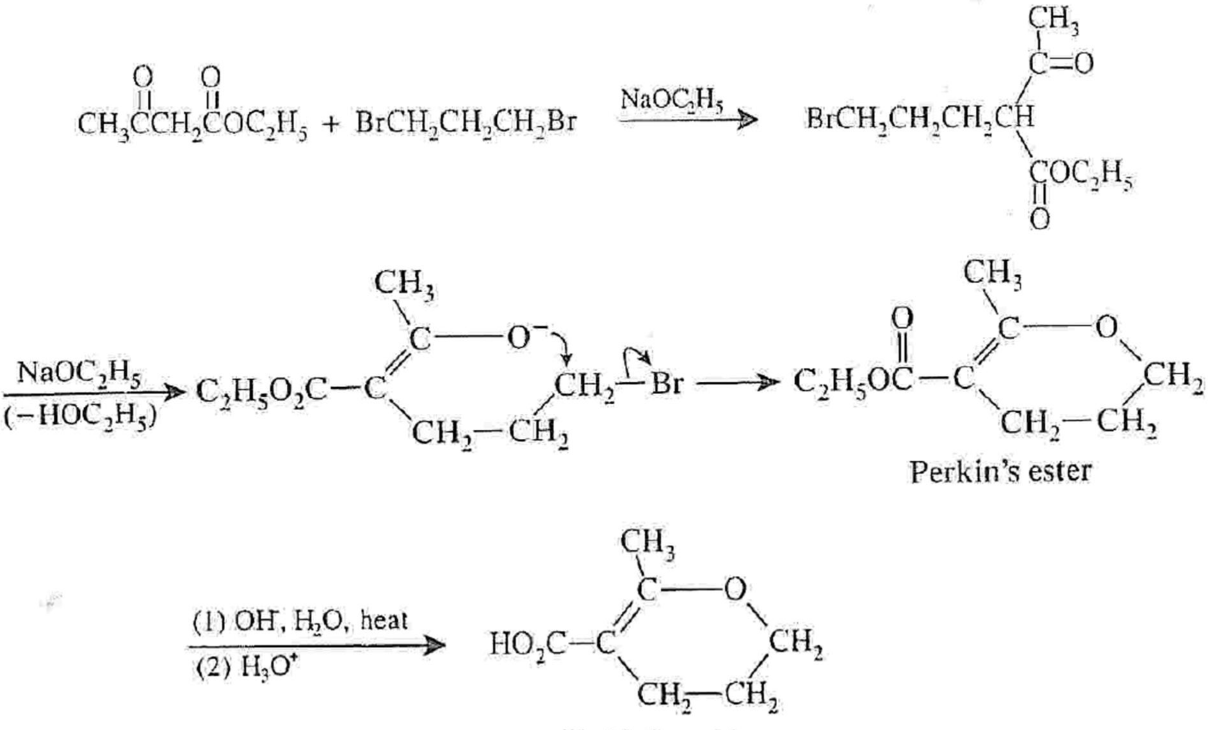


19.29 Siklobütankarboksilik asitin sentezi Altbölüm 19.4'te verilmiştir. Bu sentez 1883 yılında ilk defa William Perkin, Jr. tarafından yapılmıştır ve altı karbon atomlu halkadan daha küçük halkalı bir organik bileşiğin ilk sentezini gösterir. (O zamanlar bu tür maddelerin çok kararsız olduğu ve sentezlenemeyeceği düşünülürdü.) 1883 yılının başlarında Perkin, asetoasetik esterin 1,3-dibromopropan ile tepkimesi sonucu siklobütan türevini yanlışlıkla oluşturduğunu yayınladı. Perkin'in gerçekleştiğini düşündüğü tepkime aşağıda verilmiştir.



Perkin'in ürününün molekül formülü bundan sonraki tepkimedeki ürünün formülüne uymaktadır. Bu ürünün bazik hidrolizi ve bunu izleyen asitlendirme çok güzel asit kristalleri oluşturmuştur (molekül formülü de düşünüldüğü gibidir). Ancak asit ısıya karşı oldukça kararlıdır ve dekarboksilasyona uğramaz. Perkin daha sonra oluşan esterin ve asidin altı üyeli halka olduğunu bulmuştur (beş karbon atomu ve bir oksijen atomu içeren). Asetoasetik esterden elde edilen enolat iyonundaki yük dağılımını düşünerek Perkin'in sentezlediği ester ve asidin yapısını bulunuz.

19.29 The following reaction took place:



Perkin's ester

Perkin's acid

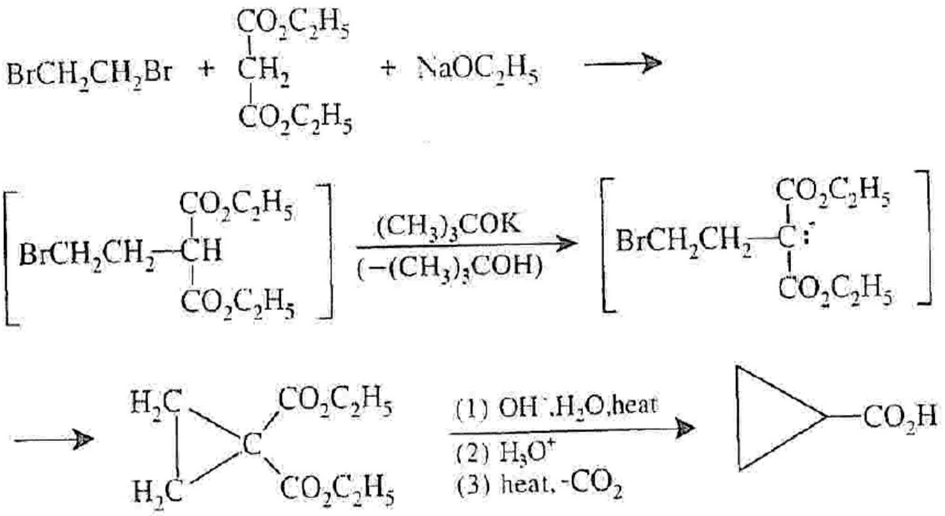
19.30 (**a**) 1884 yılında Perkin, siklopropankarboksilik asiti sodyomalonik ester ve 1,2-dibromoetandan başarılı bir sentezle elde etti. Bu sentezde oluşan tepkimeleri yazınız (**b**) 1885 yılında Perkin beş üyeli **D** ve **E** karboksil bileşiklerini aşağıdaki yolla sentezledi:

$$2\,Na^{+}:\overset{-}{C}H(CO_2C_2H_5)_2 + BrCH_2CH_2CH_2Br \longrightarrow \textbf{A}\,(C_{17}H_{28}O_8) \xrightarrow{2\,C_2H_5O^{-}Na^{+}} \xrightarrow{Br_2}$$

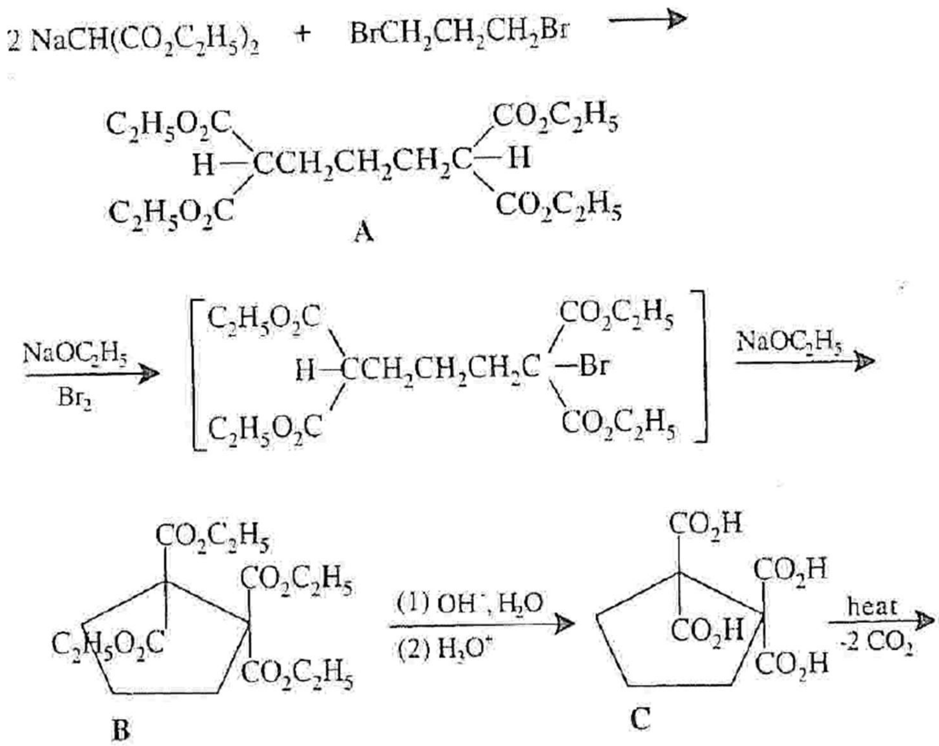
$$\textbf{B}\,(C_{17}H_{26}O_8) \xrightarrow[(2)\ H_3O^{+}]{(1)\ OH^{-}/H_2O} \textbf{C}\,(C_9H_{10}O_8) \xrightarrow{ısı} \textbf{D}\,(C_7H_{10}O_4) + \textbf{E}\,(C_7H_{10}O_4)$$

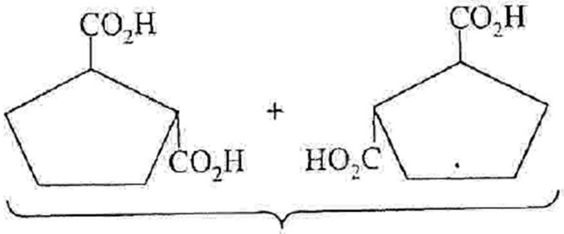
D ve **E** diastereomerlerdir; **D**, enantiyomerlerine ayrılabilir, **E** ise ayrılamaz. **A–E** bileşiklerinin yapıları nasıldır? (**c**) Perkin on yıl sonra 1,4-dibromobütan sentezledi ve bu bileşiği daha sonra dietilmalonatta etkileştirerek siklopentankarboksilik asiti hazırladı. Oluşan tepkimeleri gösteriniz.

19.30 (a)



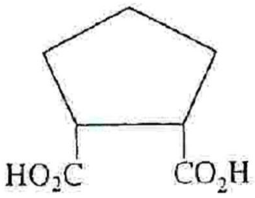
(b)





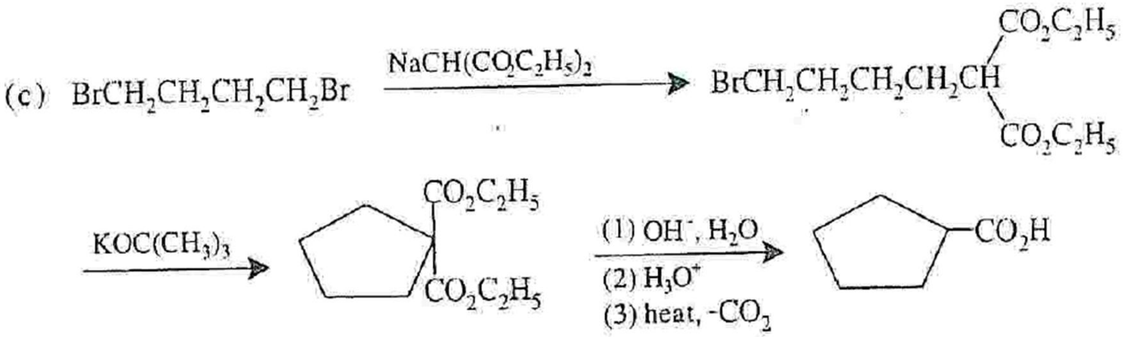
D

Racemic form

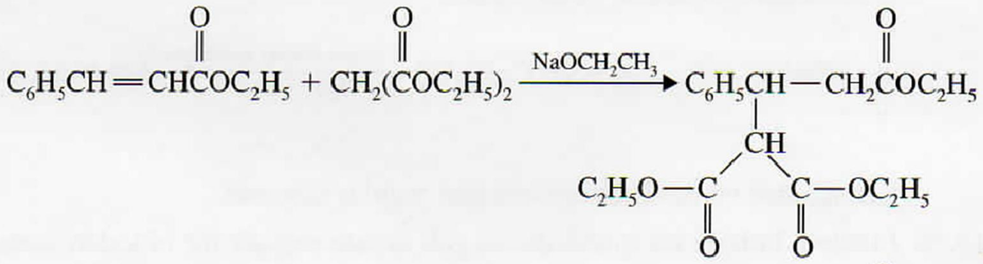


E

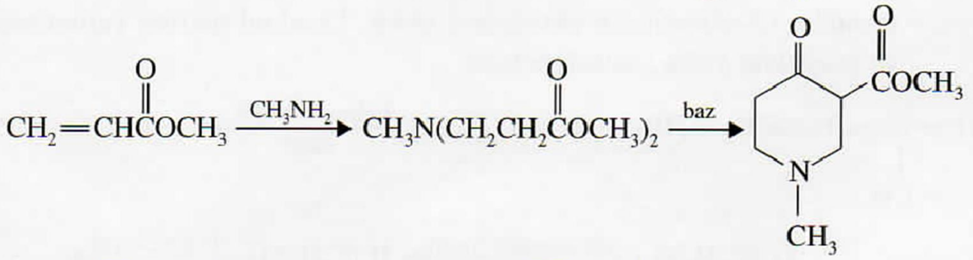
Meso compound

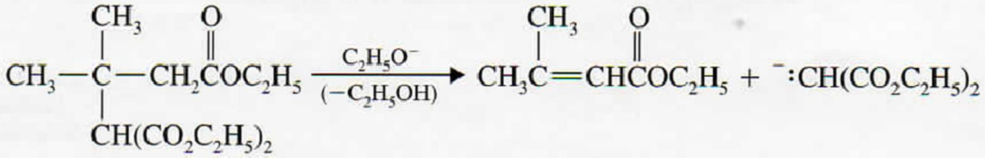


19.31 Aşağıdaki ürünleri oluşturan tepkimelerin mekanizmalarını yazınız.

(a) 

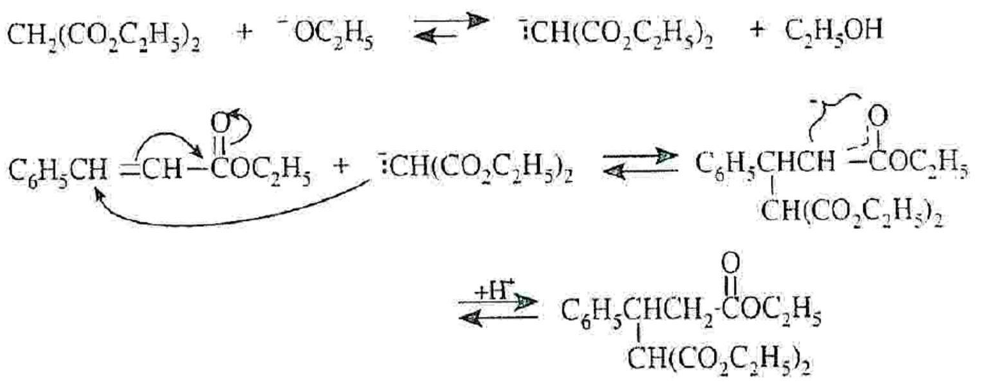
$$C_6H_5CH{=}CH\overset{O}{\overset{\|}{C}}OC_2H_5 + CH_2(\overset{O}{\overset{\|}{C}}OC_2H_5)_2 \xrightarrow{NaOCH_2CH_3} C_6H_5\underset{CH(\overset{O}{\overset{\|}{C}}OC_2H_5)_2}{CH}-CH_2\overset{O}{\overset{\|}{C}}OC_2H_5$$

(b) 

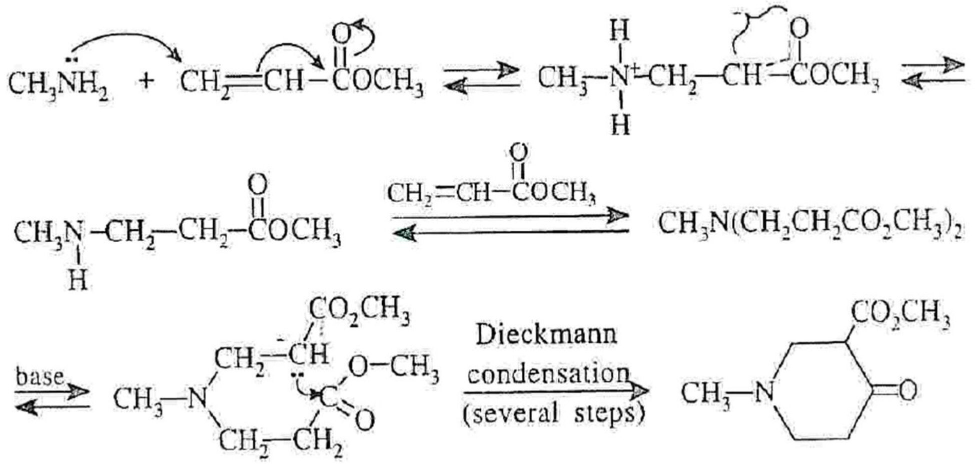
(c) 

$$CH_3-\overset{CH_3}{\underset{CH(CO_2C_2H_5)_2}{C}}-CH_2\overset{O}{\overset{\|}{C}}OC_2H_5 \xrightarrow[(-C_2H_5OH)]{C_2H_5O^-} CH_3\overset{CH_3}{C}{=}CH\overset{O}{\overset{\|}{C}}OC_2H_5 + {}^-{:}CH(CO_2C_2H_5)_2$$

19.31 (a)



(b)



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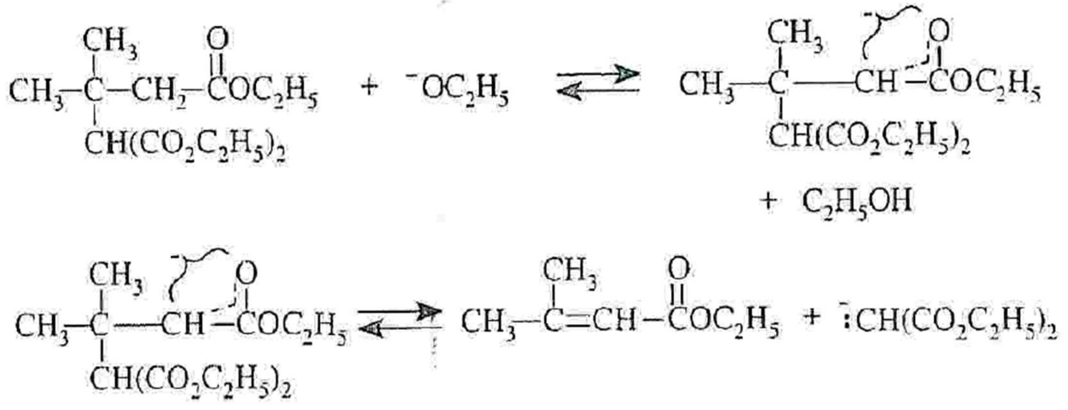
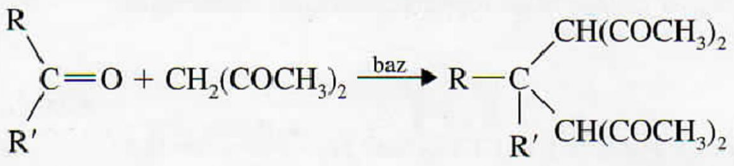


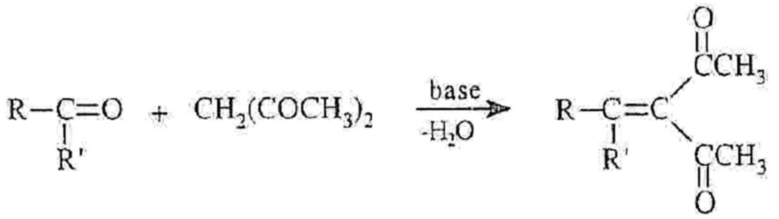
The Michael reaction is reversible, and the reaction just given is an example of a reverse Michael reaction.

19.32 Knoevenagel kondensasyonunda aktif hidrojen bileşikleri β-keto ester veya β-diketondur. Bu kondensasyon tepkimesi bir molekül aldehit veya keton, iki molekül aktif metilen bileşiği kullanılarak yapılır. Örneğin,

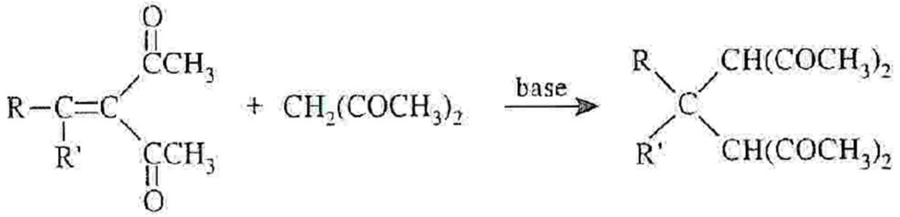


Bu ürünlerin oluşumunu açıklayan mantıklı bir mekanizma öneriniz.

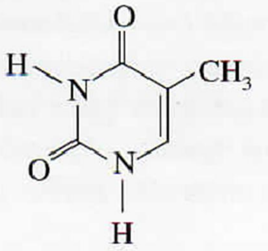
19.32 Two reactions take place. The first is a normal Knoevenagel condensation.



Then the α, β-unsaturated diketone reacts with a second mole of the active methylene compound in a Michael addition.

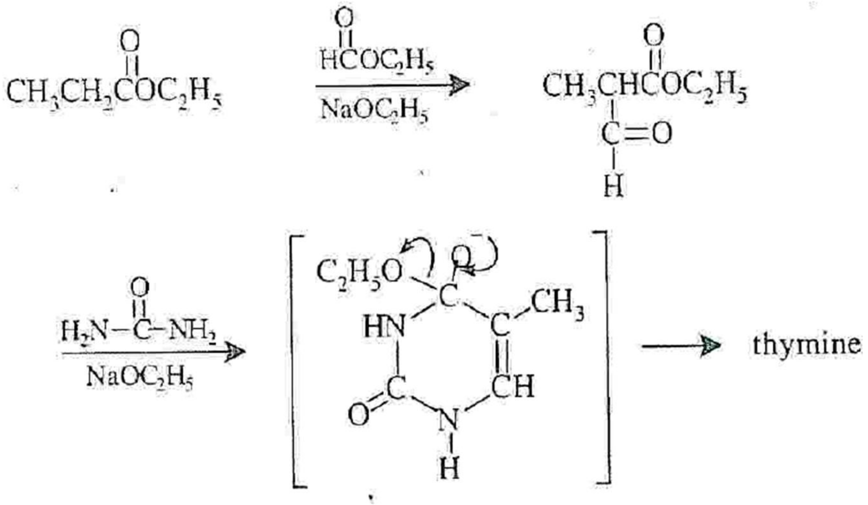


19.33 Timin bir heterosiklik bazdır ve DNA'nın yapısında bulunur. (Bölüm girişine bakınız). Etil propanoat ve gerekli bir başka reaktiften başlayarak timini nasıl sentezleyebileceğinizi gösteriniz.



Timin

19.33



19.34 Kraliçe arının salgılamış olduğu sıvı, "kraliçe özü" olarak bilinen önemli bir madde içerir. Çok az miktarda kraliçe özü işçi arılara aktarıldığında onların yumurtalıklarının gelişmesini önleyerek yeni kraliçelerin oluşmasını engeller. Kraliçe özü $C_{10}H_{16}O_3$ molekül formülüne sahip bir karboksilik asittir ve aşağıdaki yolla sentezlenir.

$$\text{Sikloheptanon} \xrightarrow[\text{(2) } H_3O^+]{\text{(1) } CH_3MgI} \mathbf{A}\ (C_8H_{16}O) \xrightarrow{\text{HA, ısı}} \mathbf{B}\ (C_8H_{14}) \xrightarrow[\text{(2) Zn, HOAc}]{\text{(1) } O_3}$$

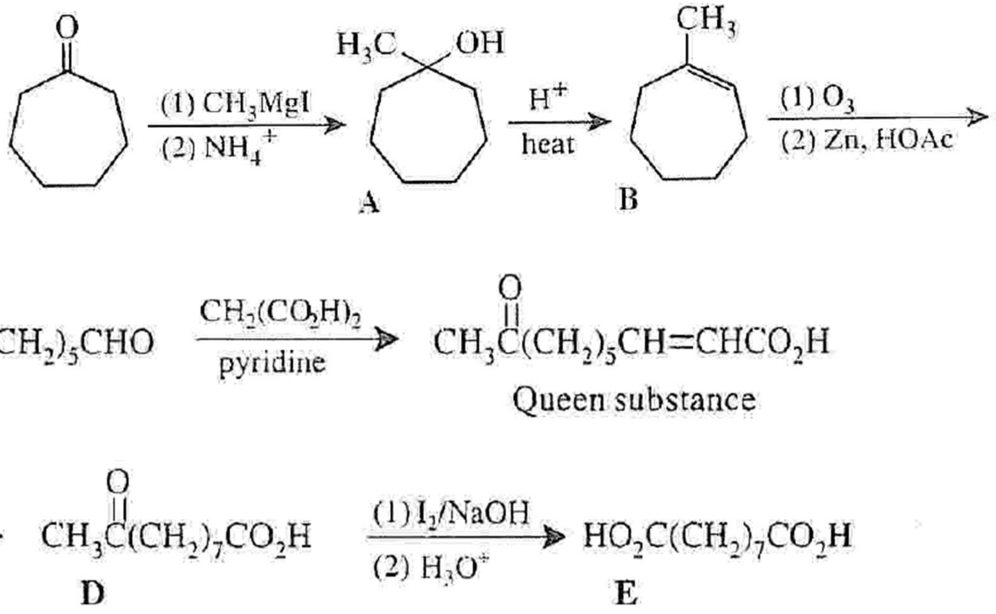
$$\mathbf{C}\ (C_8H_{14}O_2) \xrightarrow[\text{piridin}]{CH_2(CO_2H)_2} \text{kraliçe özü}\ (C_{10}H_{16}O_3)$$

Kraliçe özünün katalitik hidrojenlenmesi sonucu **D** bileşiği oluşur. Bunun sodyum hidroksit içerisindeki iyot ile etkileştirilmesi ve ardından asitlendirilmesiyle dikarboksilik asit **E** oluşur, yani;

$$\text{Kraliçe özü} \xrightarrow[\text{Pd}]{H_2} \mathbf{D}\ (C_{10}H_{18}O_3) \xrightarrow[\text{(2) } H_3O^+]{\text{(1) sulu NaOH içerisinde } I_2} \mathbf{E}\ (C_9H_{16}O_4)$$

Kraliçe özü ve **A–E** bileşikleri için yapılar öneriniz.

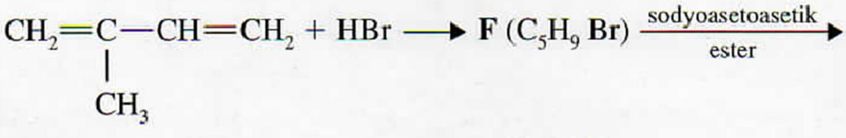
19.34



$$\underset{\mathbf{C}}{CH_3\overset{O}{\overset{\|}{C}}(CH_2)_5CHO} \xrightarrow[\text{pyridine}]{CH_2(CO_2H)_2} \underset{\text{Queen substance}}{CH_3\overset{O}{\overset{\|}{C}}(CH_2)_5CH{=}CHCO_2H}$$

$$\xrightarrow[\text{Pd}]{H_2} \underset{\mathbf{D}}{CH_3\overset{O}{\overset{\|}{C}}(CH_2)_7CO_2H} \xrightarrow[\text{(2) } H_3O^+]{\text{(1) } I_2/NaOH} \underset{\mathbf{E}}{HO_2C(CH_2)_7CO_2H}$$

19.35 Linalool kokulu bir maddedir ve çok sayıda değişik tür bitkiden izole edilebilir, formülü 3,7-dimetil-1,6-oktadien-3-oldür. Linalool parfüm yapımında kullanılır ve aşağıdaki yolla sentezlenebilir.



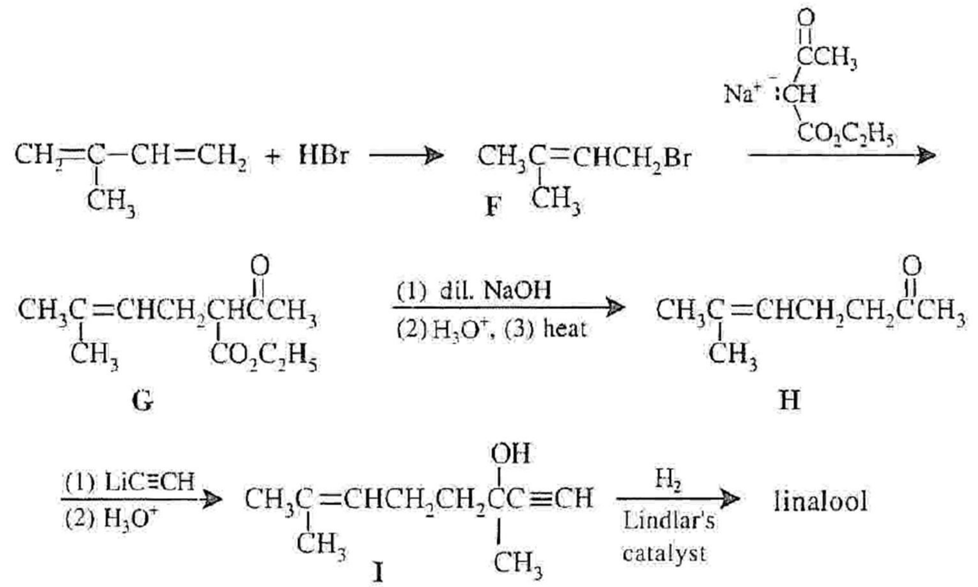
$$CH_2{=}\underset{CH_3}{\underset{|}{C}}{-}CH{=}CH_2 + HBr \longrightarrow \mathbf{F}\ (C_5H_9Br) \xrightarrow[\text{ester}]{\text{sodyoasetoasetik}}$$

$$\mathbf{G}\ (C_{11}H_{18}O_3) \xrightarrow[\text{(2) } H_3O^+\text{, (3) ısı}]{\text{(1) seyreltik NaOH}} \mathbf{H}\ (C_8H_{14}O) \xrightarrow[\text{(2) } H_3O^+]{\text{(1) LiC}{\equiv}\text{CH}}$$

$$\mathbf{I}\ (C_{10}H_{16}O) \xrightarrow[\text{Lindlar katalizörü}]{H_2} \text{linalool}$$

Oluşan tepkimeleri gösteriniz. (*İpucu:* **F** bileşiği ilk basamakta oluşabilecek ürünler içinde daha kararlı olan izomerdir.)

19.35



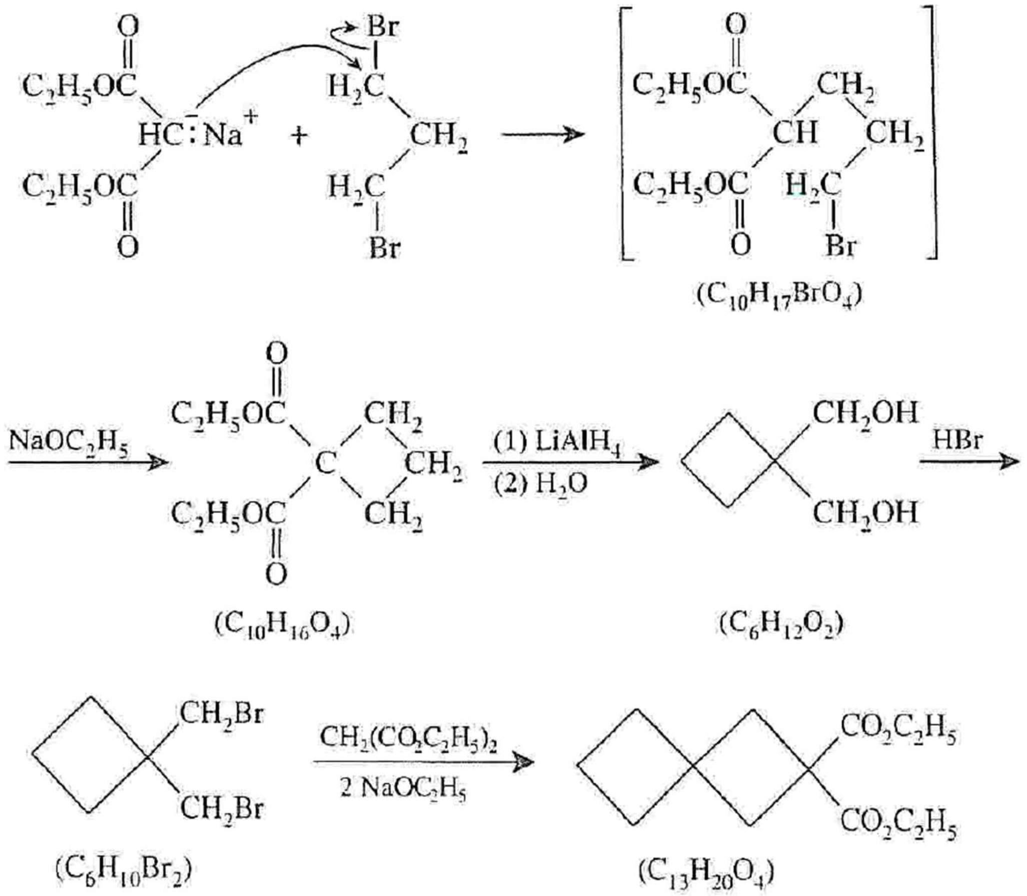
19.36 **J** bileşiği, iki tane dört üyeli halkası olan bir bileşiktir ve aşağıdaki yolla sentezlenmiştir. İçerilen basamakları gösteriniz.

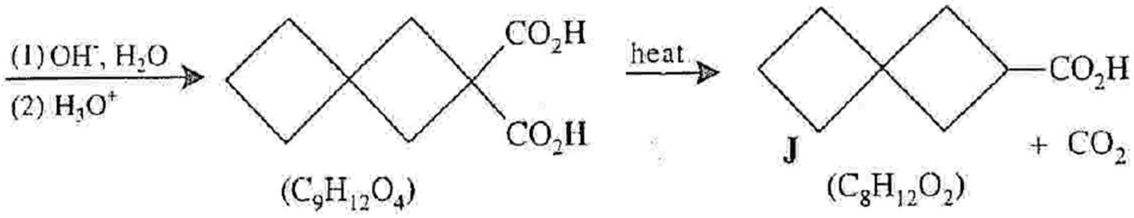
$$\mathrm{NaCH(CO_2C_2H_5)_2 + BrCH_2CH_2CH_2Br \longrightarrow (C_{10}H_{17}BrO_4) \xrightarrow{NaOC_2H_5}}$$

$$\mathrm{C_{10}H_{16}O_4 \xrightarrow[(2)\ H_2O]{(1)\ LiAlH_4} C_6H_{12}O_2 \xrightarrow{HBr} C_6H_{10}Br_2 \xrightarrow[2\ NaOC_2H_5]{CH_2(CO_2C_2H_5)_2}}$$

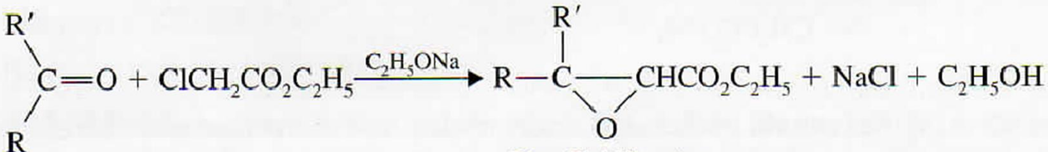
$$\mathrm{C_{13}H_{20}O_4 \xrightarrow[(2)\ H_3O^+]{(1)\ OH^-,\ H_2O} C_9H_{12}O_4 \xrightarrow{ısı} \mathbf{J}\ (C_8H_{12}O_2) + CO_2}$$

19.36



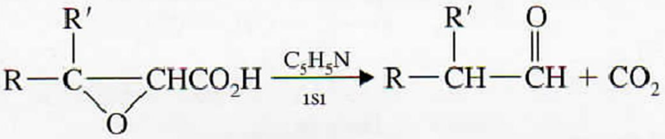


19.37 Bir aldehit veya bir keton, etil α-kloroasetat ile sodyum etoksit varlığında kondenseleştiğinde, ürün α,β-epoksi esterdir ve *glisidik ester* olarak adlandırılır. Bu sentez Darzen kondensasyonu olarak bilinir.

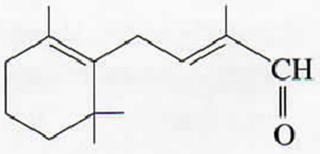

$$RR'C{=}O + ClCH_2CO_2C_2H_5 \xrightarrow{C_2H_5ONa} R{-}CR'(O)CHCO_2C_2H_5 + NaCl + C_2H_5OH$$

Bir gilisidik ester

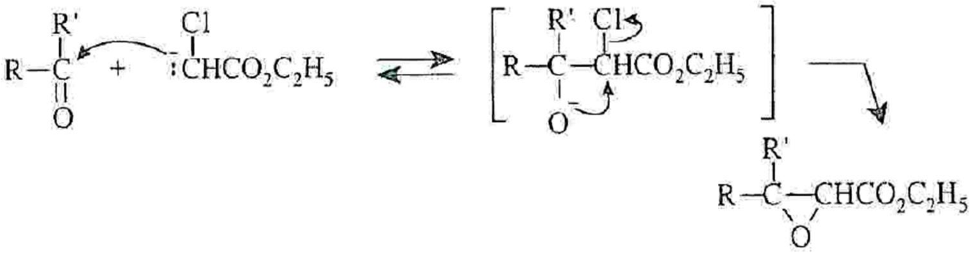
(a) Darzen kondensasyonu için uygun bir mekanizma yazınız. **(b)** Epoksi esterin hidrolizi sonucu epoksi asit oluşur, daha sonra piridin ile ısıtıldığında bir aldehit verir. Burada ne olmaktadır?


$$R{-}CR'(O)CHCO_2H \xrightarrow[\text{ısı}]{C_5H_5N} R{-}CHR'{-}CH{=}O + CO_2$$

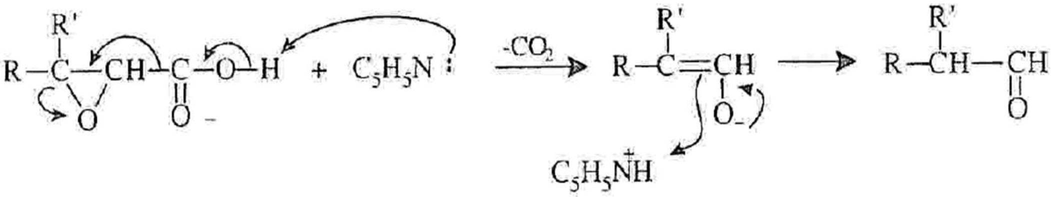
(c) β-iyononla başlayarak (Problem 17.13) aşağıdaki aldehiti nasıl sentezleyebileceğini gösteriniz. (Bu aldehit A vitamininin endüstriyel sentezinde bir ara üründür.)



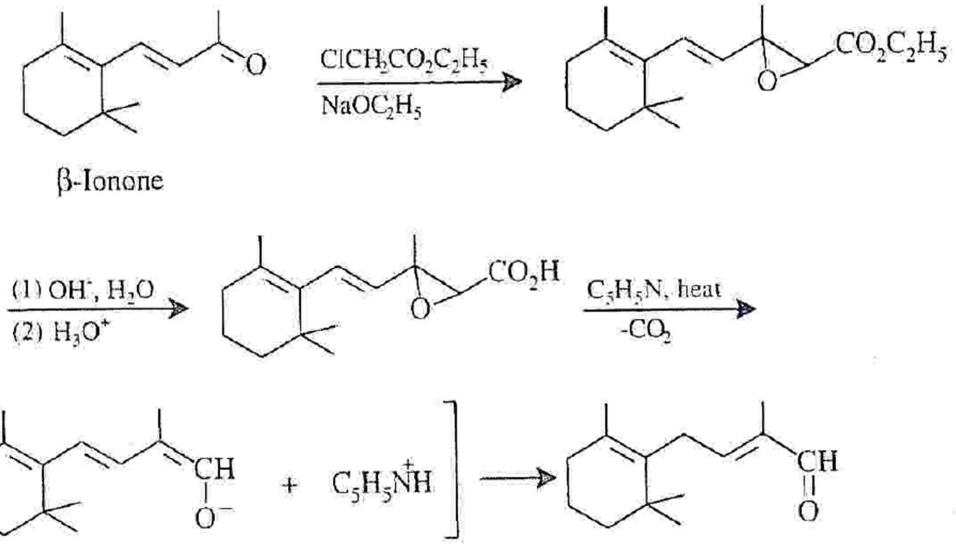
19.37 (a) $ClCH_2CO_2C_2H_5 + C_2H_5O^- \rightleftharpoons Cl-\overset{-}{\ddot{C}}HCO_2C_2H_5 + C_2H_5OH$



(b) Decarboxylation of the epoxy acid gives an enol anion which, on protonation, gives an aldehyde.

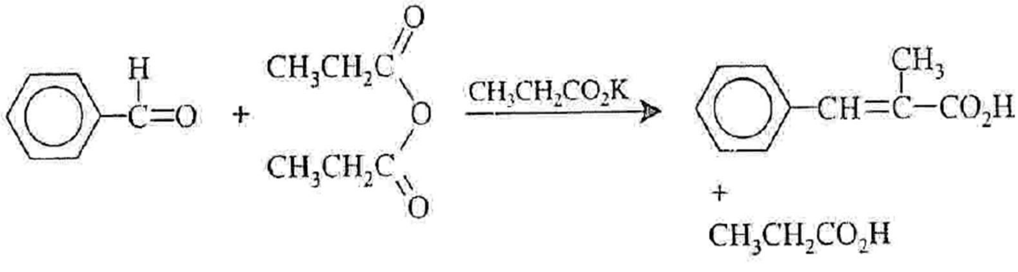


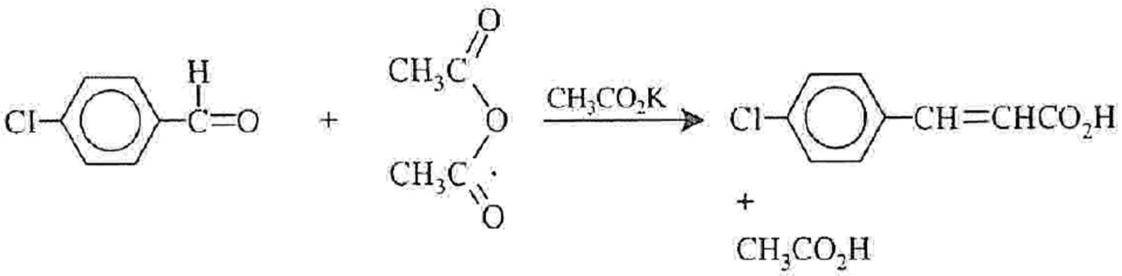
(c)



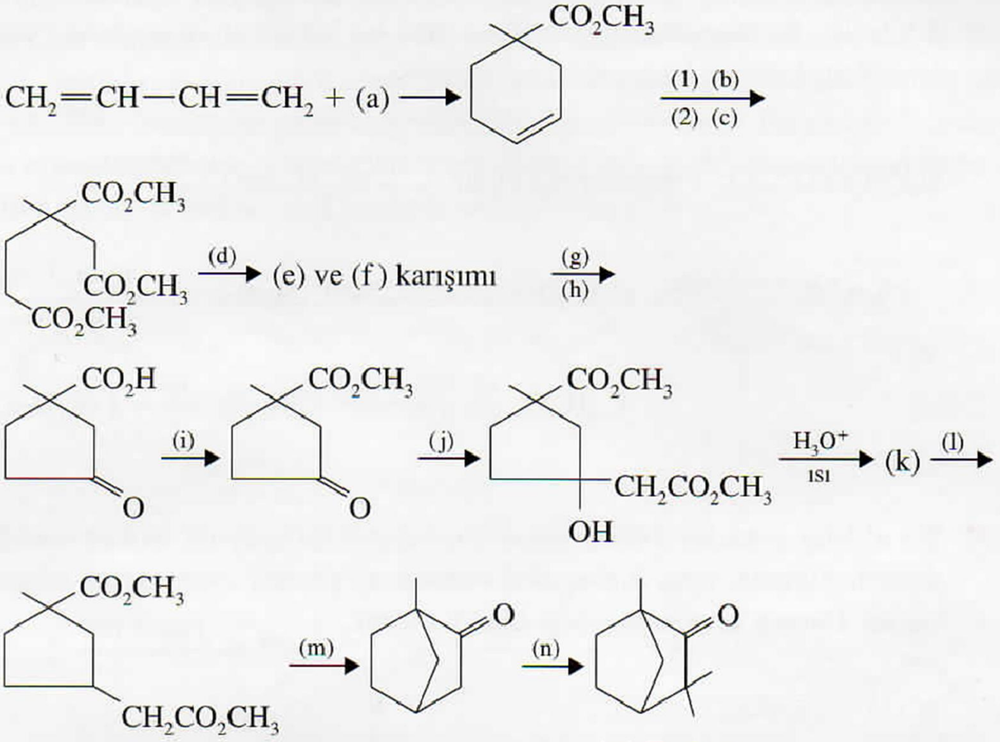
19.38 *Perkin kondensasyonu* bir aldol türü kondensasyondur. Bu tepkimede bir aromatik aldehit (ArCHO) bir karboksilik anhidritle $(RCH_2CO)_2O$ tepkimeye girer ve bir α,β-doymamış asit ($ArCH{=}CRCO_2H$) verir. Katalizör olarak karboksilik asidin potasyum tuzu (RCH_2CO_2K) kullanılır. **(a)** Benzaldehit, propiyonik anhidrit ile potasyum propanoat varlığında tepkimeye girdiğinde oluşan Perkin kondensasyonunu gösteriniz. **(b)** *p*-Klorosinamik asidi (p-$ClC_6H_4CH{=}CHCO_2H$) Perkin kondensasyon tepkimesiyle nasıl elde edersiniz?

19.38 (a)

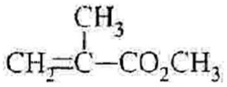


(b) 

19.39 (+)-Fenkon bir terpenoittir ve rezene (padişah otu) yağından izole edilir. (±)Fenkon aşağıdaki yolla sentezlenmiştir. Yazılmayan ara ürün ve reaktifleri yazınız.



(±)-Fenkon

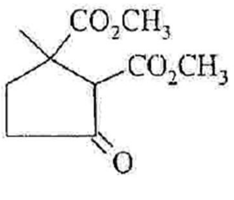
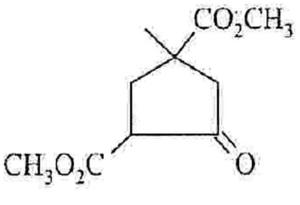
19.39 (a) 

$$CH_2{=}\overset{CH_3}{\underset{}{C}}{-}CO_2CH_3$$

(b) $KMnO_4$, OH^-, then H_3O^+

(c) CH_3OH, H^+

(d) CH_3ONa, then H^+

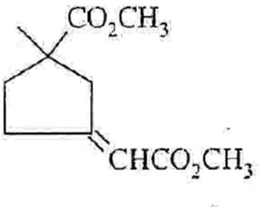
(e) and (f)  and 

(g) OH^-, H_2O, then H_3O^+

(h) heat ($-CO_2$)

(i) CH_3OH, H^+

(j) $BrCH_2CO_2CH_3$, Zn, then H_3O^+

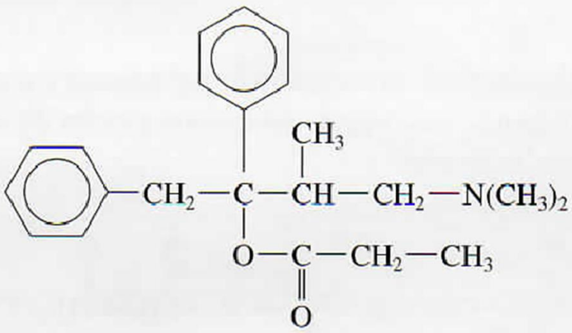
(k) 

(l) H_2, Pt

(m) CH_3ONa, then H^+

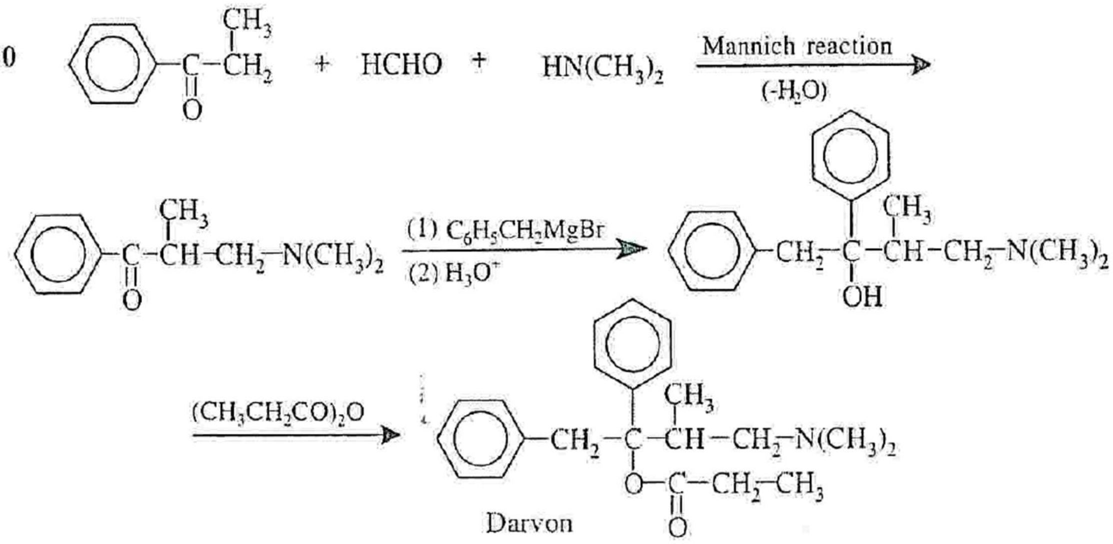
(n) 2 $NaNH_2$ + 2 CH_3I

19.40 Aşağıda formülü verilen ağrı kesici madde olan Darvonun sentezini etil fenil ketondan çıkarak tasarlayınız.



Darvon

19.40



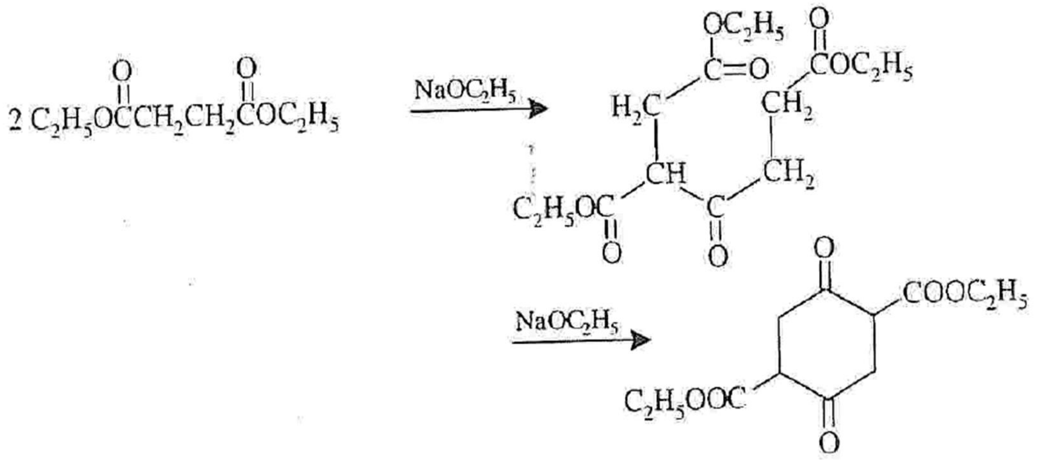
19.41 Asetilasetonun (2,4-pentandion) aşağıda verilen farklı çözeltiler içerisindeki enol miktarlarının değişimini açıklayınız.

Çözücü	**%Enol**
H_2O	15
CH_3CN	58
C_6H_{14}	92
gaz fazı	92

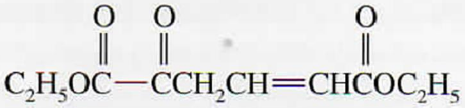
19.41 In a polar solvent, such as water, the keto form is stabilized by solvation. When the interaction with the solvent becomes minimal, the enol form achieves stability by internal hydrogen bonding.

19.42 Dietil süksinata Dieckmann kondensasyonu uygulandığında elde edilen ürünün molekül formülü $C_{12}H_{16}O_6$'dır. Bu bileşiğin yapısını bulunuz.

19.42 Intramolecular cyclization (which would give a product of formula $C_6H_8O_3$) is not favored because of ring strain. The formula of the product actually obtained suggests a 1:1 intermolecular reaction:



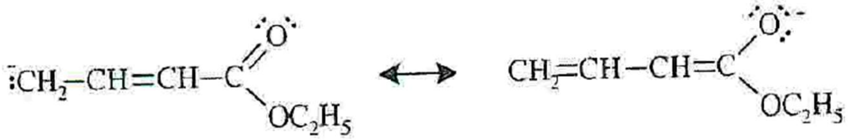
19.43 Etil krotonat, $CH_3CH{=}CHCOOC_2H_5$, dietil oksalatla, $C_2H_5OOCCOOC_2H_5$, tepkimeye girdiğinde Claisen türü bir kondensasyon ürünü verir.



$$C_2H_5O\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}CH_2CH{=}CH\overset{O}{\overset{\|}{C}}OC_2H_5$$

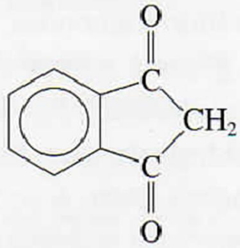
Bu bileşiğin oluşmasını gösteren ayrıntılı mekanizmayı yazınız.

19.43 A gamma hydrogen is abstracted by base (as is an alpha hydrogen in the usual Claisen) to give a resonance-stabilized species:

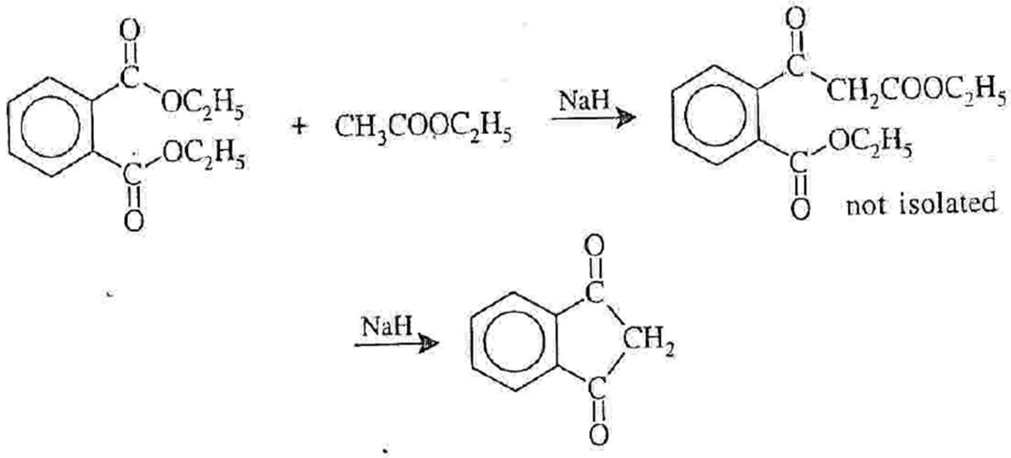


Ethyl crotonate differs from ethyl acetate by $-CH{=}CH-$, a vinyl group. The transmission of the stabilizing effect of the $-COOC_2H_5$ group is an example of the **principle of vinylogy.**

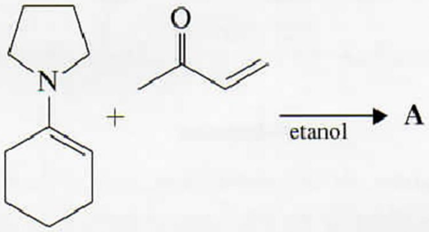
19.44 Aşağıdaki diketonun bir kondensasyon tepkimesiyle nasıl elde edileceğini gösteriniz.



19.44 The synthesis actually involves two sequential Claisen condensations, with ethyl acetate serving as the source of the carbanionic species.



***19.45 (a)** Oldukça simetrik yapıda olan **A** bileşiğinin yapısını bulunuz.



Aşağıda **A** bileşiği için seçilmiş spektrum verileri verilmiştir.

MS (m/z): 220 ($M^{+\cdot}$)

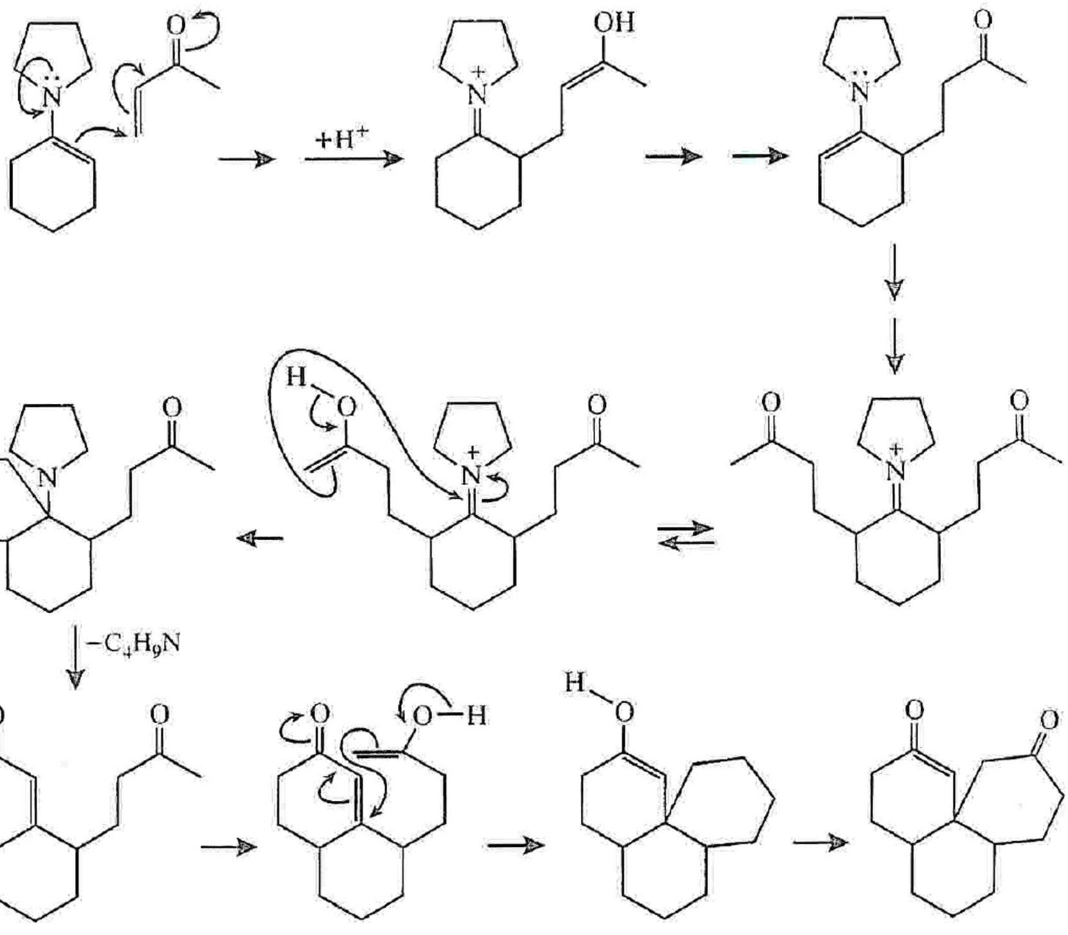
İR (cm^{-1}): 2930, 2860, 1715

^{1}**H NMR** (δ): 1,25 (ç); 1,29 (ç); 1,76 (ç); 1,77 (ç); 2,14 (b) ve 2,22 (ü) (sırasıyla , integral oranları 2 : 1 : 2 : 1 : 2 : 2)

^{13}**C NMR** (δ): 23 (CH_2), 26 (CH_2), 27 (CH_2), 29 (C), 39 (CH), 41 (CH_2), 46 (CH_2) 208 (C)

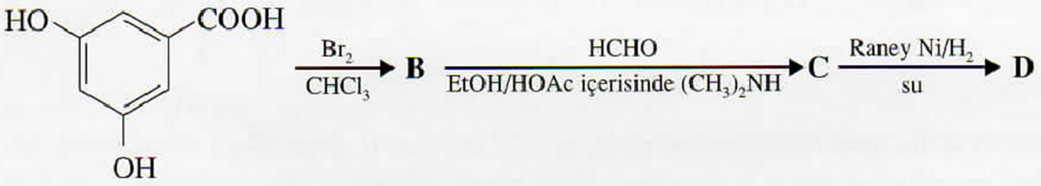
(b) A bileşiğinin oluşumunu açıklayan bir mekanizma yazınız?

*19.45



A

***19.46** Aşağıda verilen tepkimede meydana gelen **B, C** ve **D** maddelerinin yapılarını yazınız.



B'nin spektrum verileri:
MS (m/z): 314, 312, 310 (bağıl bolluk 1 : 2 : 1)
^{1}**H NMR** (δ): D_2O ile etkileştirildikten sonra, yalnızca 6,80 (b)

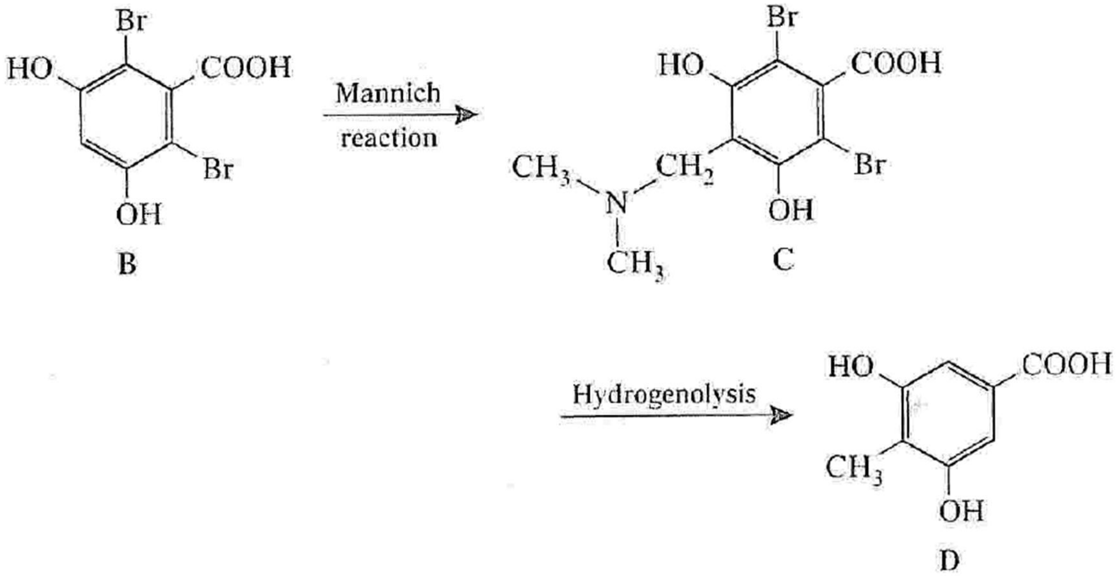
C için veriler:

MS (m/z): 371, 369, 367 (bağıl bolluk 1 : 2 : 1)
1H NMR (δ): 2,48 (b) ve 4,99 (b); alan oranı 3 : 1; D_2O ile etkileştirildikten sonra 5,5 ve 11'deki geniş birliler yok oldu.

D nin verileri:

MS (m/z): 369 ($M^{+\cdot} - CH_3$) [tris(trimetilsilil) türevleriyle çalışıldığında]
^{1}**H NMR** (δ): 2,16 (b) ve 7,18 (b); alan oranları 3 : 2; D_2O ile etkileştrildikten sonra 5,4 ve 11'deki geniş birliler kayboldu.

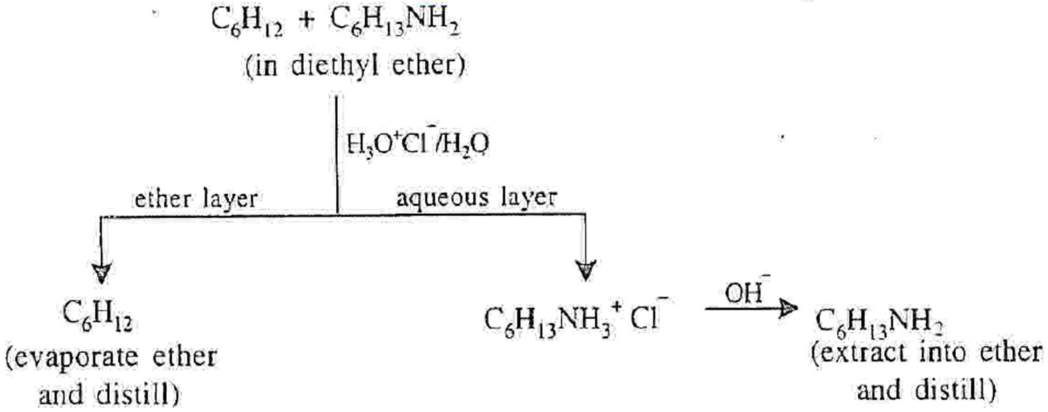
*19.46



Aminler

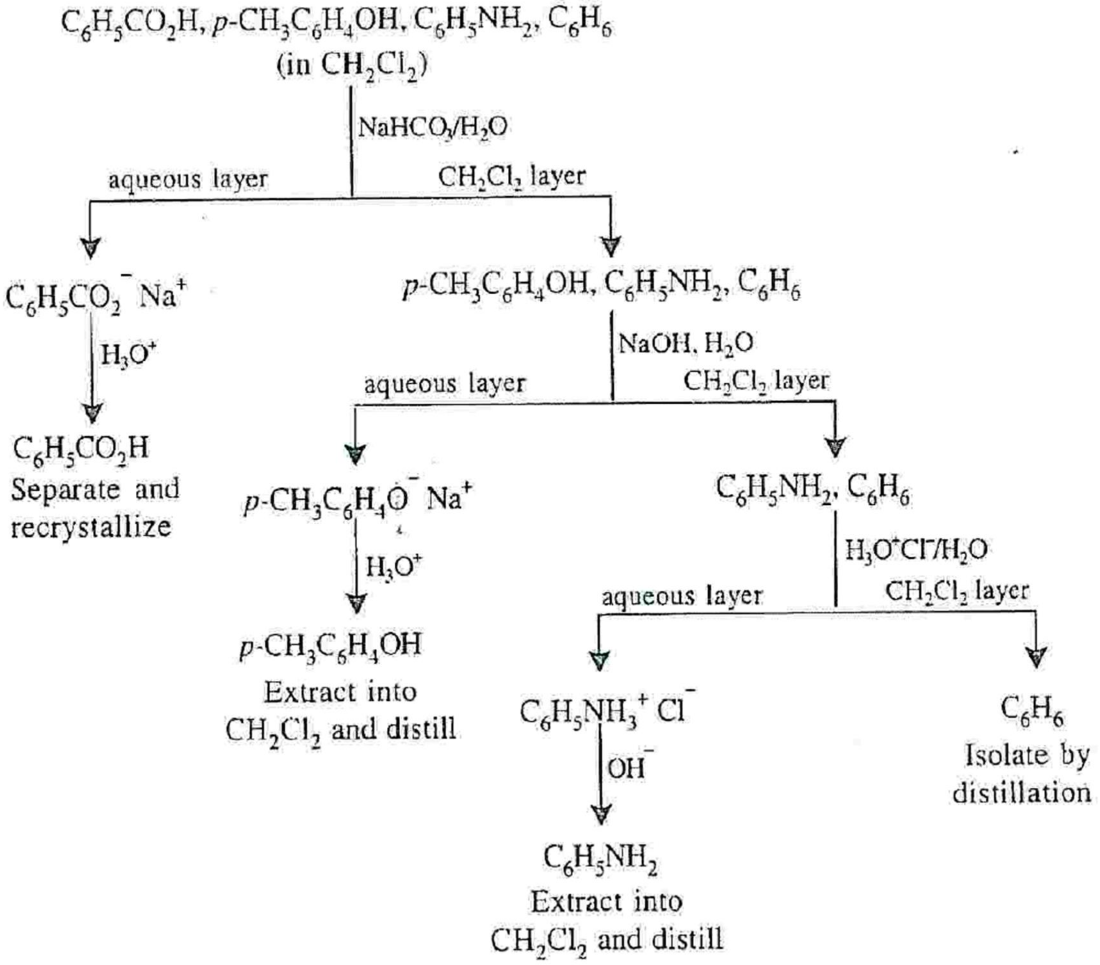
Problem 20.1 ➤ Heksilamini sikloheksandan ayırmak için seyreltik HC1, sulu NaOH ve dietil eterden yararlanarak bir yöntem geliştiriz.

20.1 Dissolve both compounds in diethyl ether and extract with aqueous HCl. This procedure gives an ether layer that contains cyclohexane and an aqueous layer that contains hexylaminium chloride. Cyclohexane may then be recovered from the ether layer by distillation. Hexylamine may be recovered from the aqueous layer by adding aqueous NaOH (to convert hexylaminium chloride to the hexylamine) and then by ether extraction and distillation.



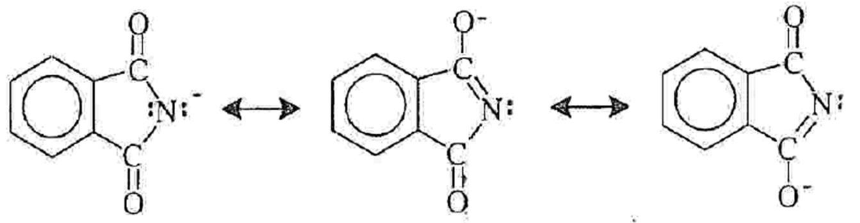
Problem 20.2 ➤ Benzoik asit, p-kresol, anilin ve benzen içeren bir karışımı, asitler, bazlar ve organik çözücüler kullanarak nasıl ayırırsınız?

20.2 We begin by dissolving the mixture in a water-immiscible organic solvent such as CH_2Cl_2 or diethyl ether. Then, extractions with aqueous acids and bases allow us to separate the components. [We separate 4-methylphenol (*p*-cresol) from benzoic acid by taking advantage of benzoic acid's solubility in the more weakly basic aqueous $NaHCO_3$, whereas *p*-cresol requires the more strongly basic, aqueous NaOH.]



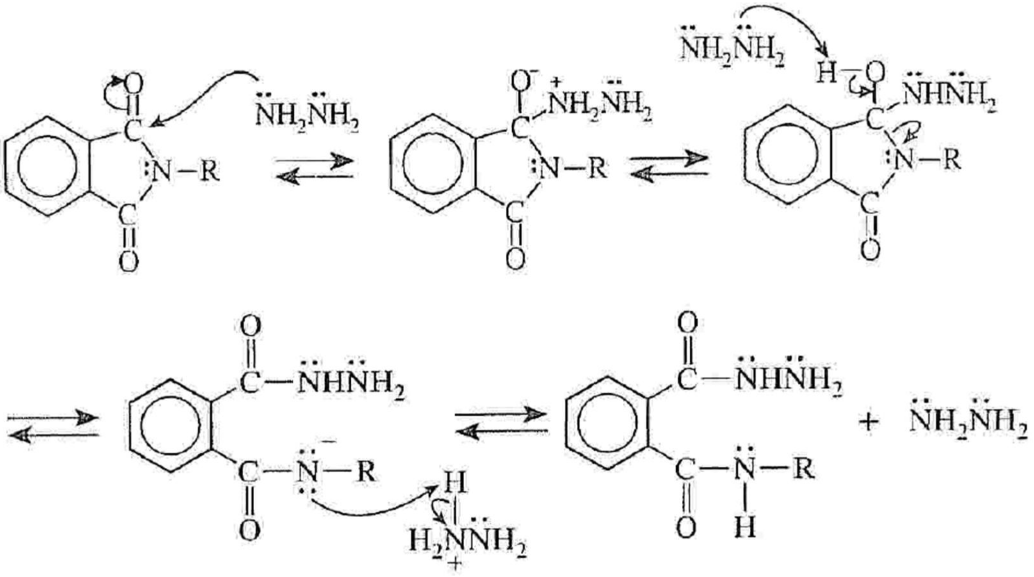
Problem 20.3 ➤ Ftalimitin asit özelliği göstermesinin başlıca nedeni, ftalimit iyonunun rezonans yapılarına sahip olmasıdır. (a) Ftalimit iyonunun rezonans yapılarını yazınız. (b) Ftalimitin asitliğini benzamitin asitliği ile karşılaştırınız. Hangisi daha güçlü asittir, neden? (c) Gabriel sentezinde 2. basamaktan sonra çeşitli basamaklar gösterilmiştir. Bu basamaklar için kabul edilebilir mekanizmalar öneriniz.

20.3 (a) Neglecting Kekulé forms of the ring, we can write the following resonance structures for the phthalimide anion.

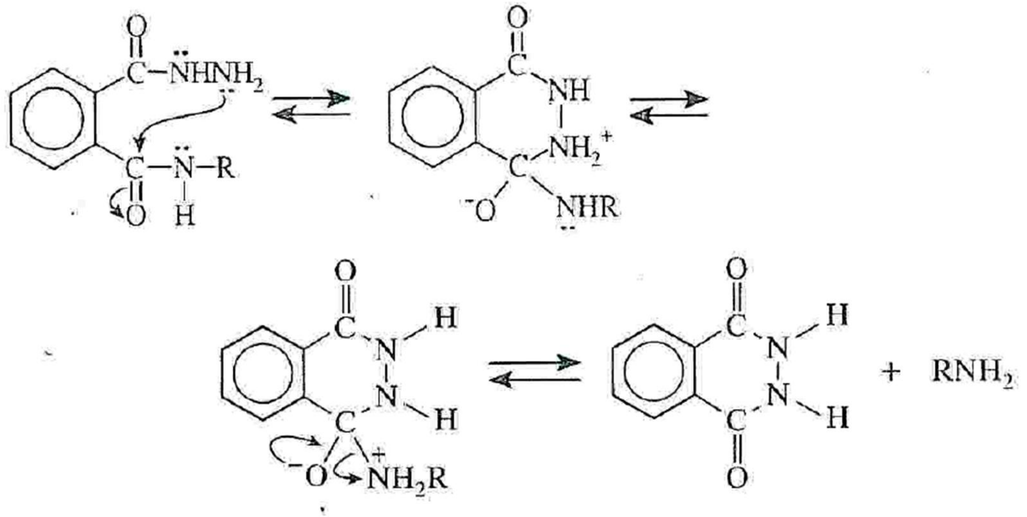


(b) Phthalimide is more acidic than benzamide because its anion is stabilized by resonance to a greater extent than the anion of benzamide. (Benzamide has only one carbonyl group attached to the nitrogen atom, and thus fewer resonance contributors are possible.)

(c)

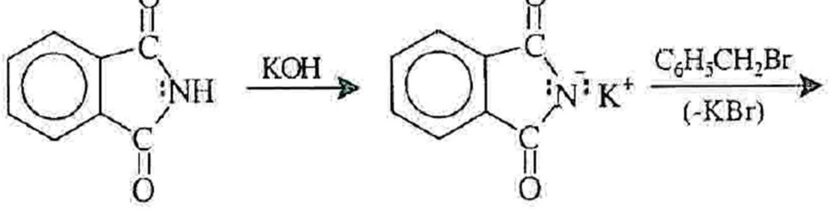


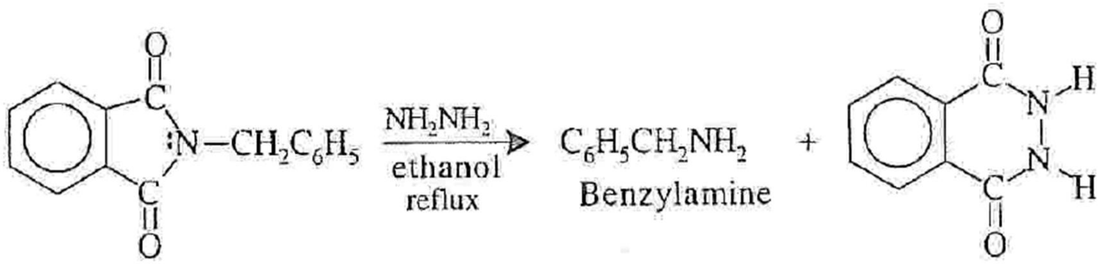
Then,



Problem 20.4 ➤ Gabriel sentezi ile benzilamin elde ediniz.

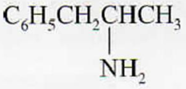
20.4





Problem 20.5 Aşağıdaki aminleri indirgeyerek aminleme yöntemiyle nasıl sentezleyebileğinizi gösteriniz.

(a) $CH_3(CH_2)_3CH_2NH_2$

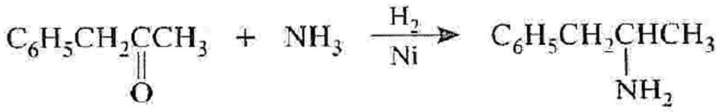
(b) 
$C_6H_5CH_2\underset{\underset{NH_2}{|}}{C}HCH_3$

(Amfetamin)

(c) $CH_3(CH_2)_4CH_2NHC_6H_5$

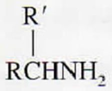
(d) $C_6H_5CH_2N(CH_3)_2$

20.5 (a) $CH_3(CH_2)_3CHO + NH_3 \xrightarrow[Ni]{H_2} CH_3(CH_2)_3CH_2NH_2$

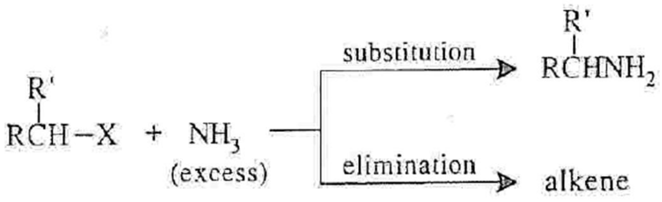
(b) 
$C_6H_5CH_2\underset{\underset{O}{\|}}{C}CH_3 + NH_3 \xrightarrow[Ni]{H_2} C_6H_5CH_2\underset{\underset{NH_2}{|}}{C}HCH_3$

(c) $CH_3(CH_2)_4CHO + C_6H_5NH_2 \xrightarrow[CH_3OH]{LiBH_3CN} CH_3(CH_2)_4CH_2NHC_6H_5$

(d) $C_6H_5CHO + (CH_3)_2NH \xrightarrow[CH_3OH]{LiBH_3CN} C_6H_5CH_2N(CH_3)_2$

Problem 20.6 
$R\overset{\overset{R'}{|}}{C}HNH_2$ tipindeki aminlerin eldesinde ketonların indirgen aminlenmesi, alkil halojenürlerin amonyakla etkileştirilmesinden daha iyi bir yöntemdir. Neden?

20.6 The reaction of a secondary halide with ammonia would inevitably be accompanied by considerable elimination, thus decreasing the yield.



Problem 20.7 Aşağıdaki dönüşümleri bir amit, oksim ya da nitrillerin indirgenmesinden yararlanarak nasıl gerçekleştirebilirsiniz?

(a) Benzoik asit ⟶ benziletilamin
(b) 1-Bromopentan ⟶ heksilamin
(c) Propanoik asit ⟶ tripropilamin
(d) Bütanon ⟶ *sek*-bütilamin

20.7 (a) $C_6H_5CO_2H \xrightarrow{SOCl_2} C_6H_5COCl \xrightarrow{CH_3CH_2NH_2}$

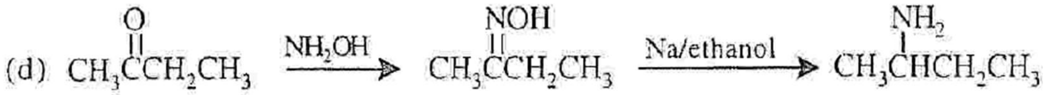
$C_6H_5CONHCH_2CH_3 \xrightarrow{LiAlH_4} C_6H_5CH_2NHCH_2CH_3$

(b) $CH_3CH_2CH_2CH_2CH_2Br \xrightarrow{NaCN} CH_3CH_2CH_2CH_2CH_2CN$

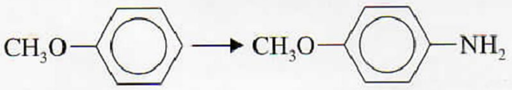
$\xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2CH_2CH_2NH_2$

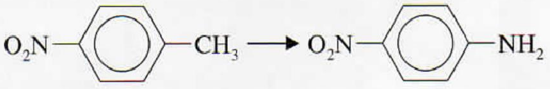
(c) $CH_3CH_2CO_2H \xrightarrow{SOCl_2} CH_3CH_2COCl \xrightarrow{(CH_3CH_2CH_2)_2NH}$

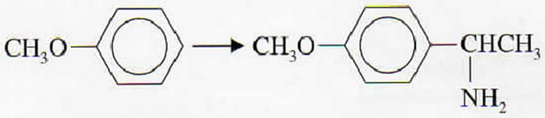
$CH_3CH_2CON(CH_2CH_2CH_3)_2 \xrightarrow{LiAlH_4} N(CH_2CH_2CH_3)_3$

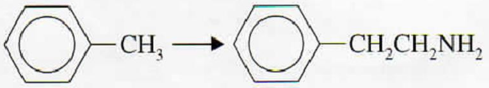

(d) $CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3 \xrightarrow{NH_2OH} CH_3\overset{\overset{NOH}{\|}}{C}CH_2CH_3 \xrightarrow{Na/ethanol} CH_3\overset{\overset{NH_2}{|}}{C}HCH_2CH_3$

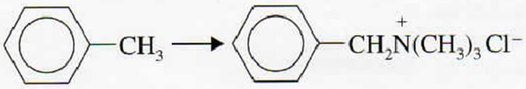
Problem 20.8 ➤ Aşağıdaki dönüşümleri, her biri için farklı ve en iyi yöntemi kullanarak gerçekleştiriniz:

(a)


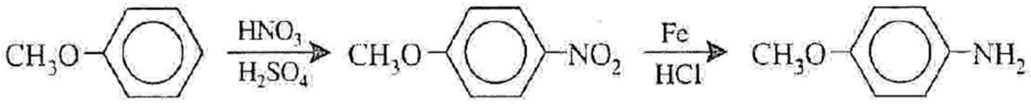
(d)


(b)


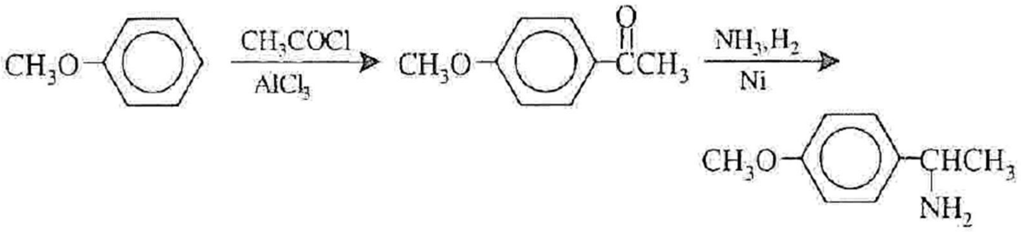
(e)


(c)


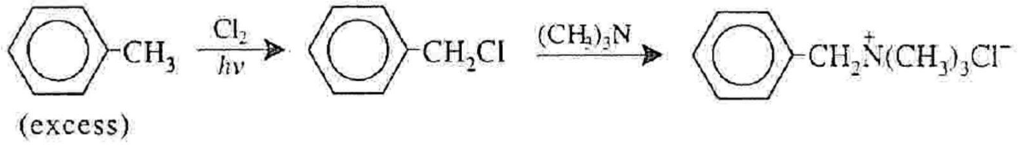
20.8 (a)



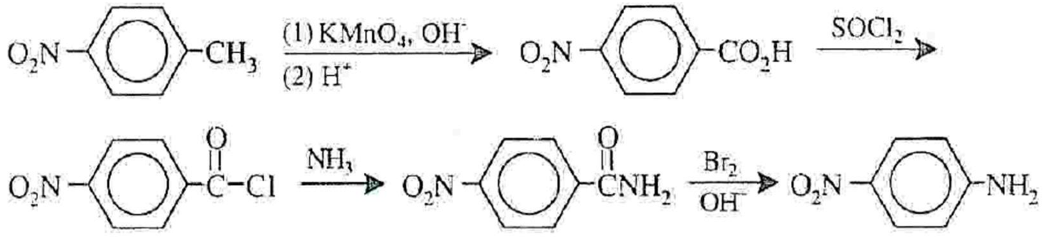
(b)



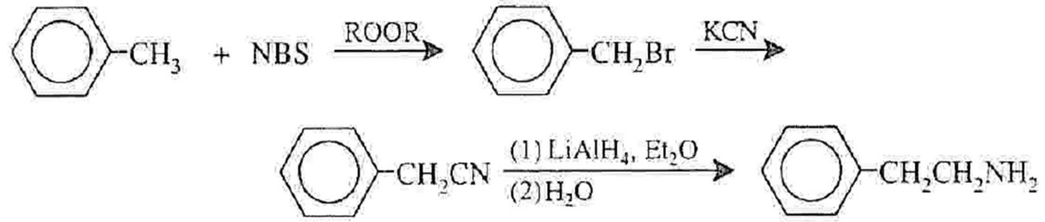
(c)



(d)

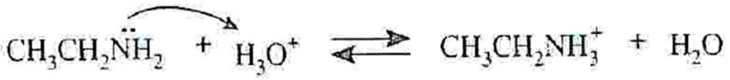


(e)



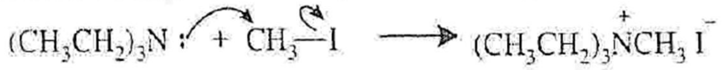
Önceki kısımlarda verilen amin kimyasını gözden geçiriniz ve yukarıda belirtilen tepkimelere örnekler veriniz. ➤ **Problem 20.9**

20.9 An amine acting as a base.



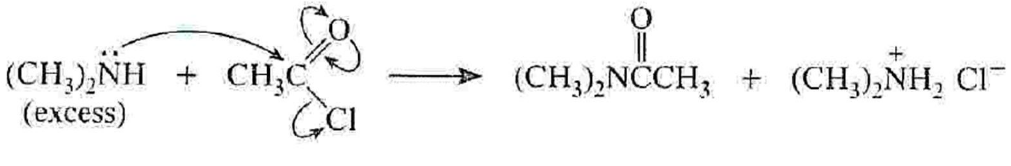
$$CH_3CH_2\ddot{N}H_2 + H_3O^+ \rightleftharpoons CH_3CH_2NH_3^+ + H_2O$$

An amine acting as a nucleophile in an alkylation reaction.



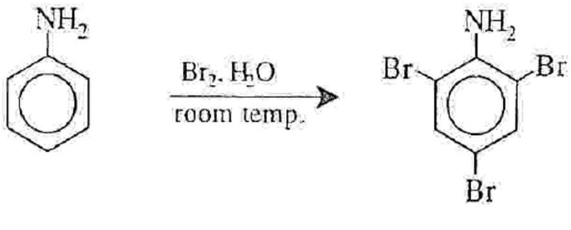
$$(CH_3CH_2)_3N: + CH_3{-}I \longrightarrow (CH_3CH_2)_3\overset{+}{N}CH_3\ I^-$$

An amine acting as a nucleophile in an acylation reaction.



$$\underset{\text{(excess)}}{(CH_3)_2\ddot{N}H} + CH_3\overset{O}{\overset{\|}{C}}Cl \longrightarrow (CH_3)_2N\overset{O}{\overset{\|}{C}}CH_3 + (CH_3)_2\overset{+}{N}H_2\ Cl^-$$

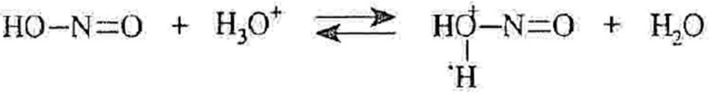
An amino group acting as an activating group and as an ortho-para director in electrophilic aromatic substitution.



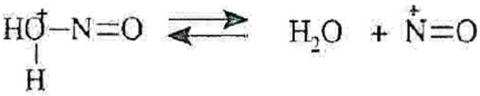
Problem 20.10

N,N-Dimetilanilinin para-nitrozolanmasının (*C*-nitrozolanması), $\overset{+}{N}O$ iyonlarının elektrofilik atağı ile yürüdüğüne inanılmaktadır. (a) $NaNO_2$ ve HCl'nin sulu çözeltisinde $\overset{+}{N}O$ iyonlarının nasıl meydana geldiğini gösteriniz. (b) *N,N*-Dimetilanilinin *p*-nitrozolanma mekanizmasını yazınız. (c) Üçüncül aromatik aminler ve fenoller *C*-nitrozolanma verirler. Oysa diğer benzen türevleri vermezler. Bu farkı nasıl açıklarsınız.

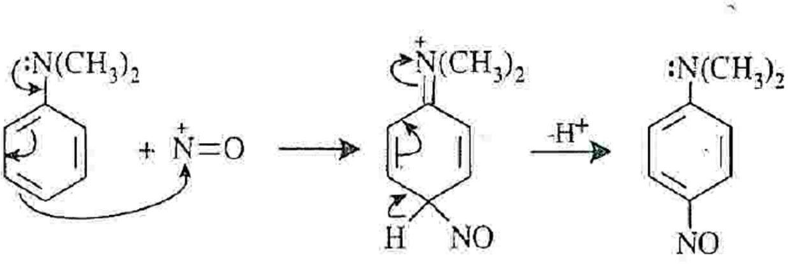
20.10 (a, b) $^{-}O-N=O + H_3O^+ \rightleftharpoons HO-N=O + H_2O$



$$HO-N=O + H_3O^+ \rightleftharpoons \underset{H}{H\overset{+}{O}}-N=O + H_2O$$



$$\underset{H}{H\overset{+}{O}}-N=O \rightleftharpoons H_2O + \overset{+}{N}=O$$



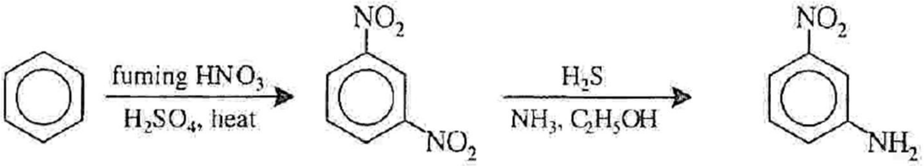
(c) The $\overset{+}{N}O$ ion is a weak electrophile. For it to react with an aromatic ring, the ring must have a powerful activating group such as –OH or $-NR_2$.

Problem 20.11

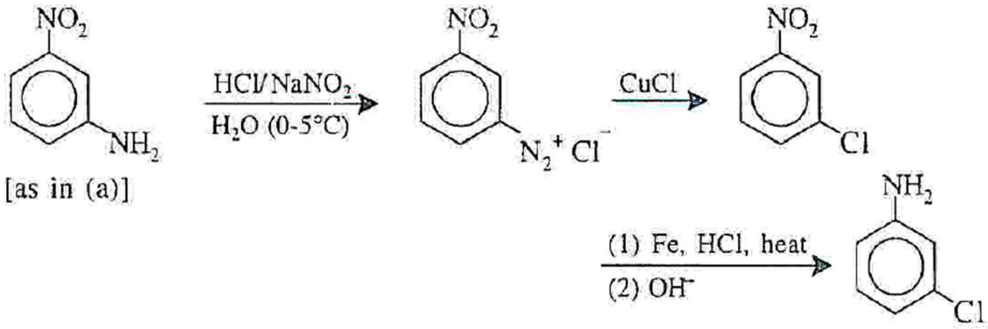
Yukarıda diazonyum tepkimelerine verdiğimiz örneklerde sentezlere (a)–(e) bileşiklerinden başladık. Aşağıda verilen bileşikleri benzenden çıkarak nasıl sentezlersiniz?

(a) *m*-Nitroanilin
(b) *m*-Kloroanilin
(c) *m*-Bromoanilin
(d) *o*-Nitroanilin
(e) *p*-Nitroanilin

20.11 (a)

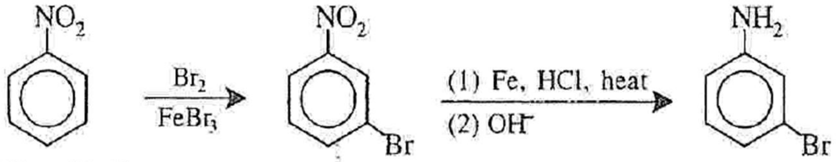


(b)



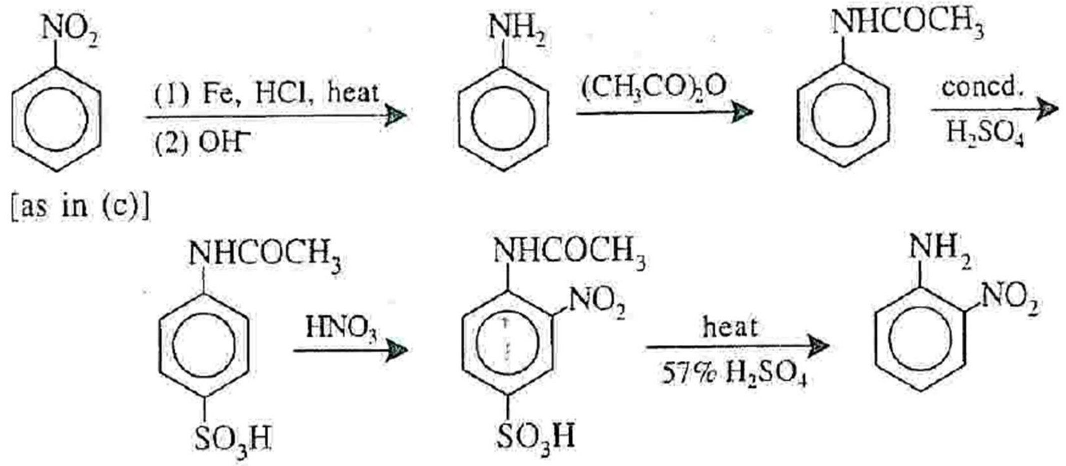
[as in (a)]

(c)

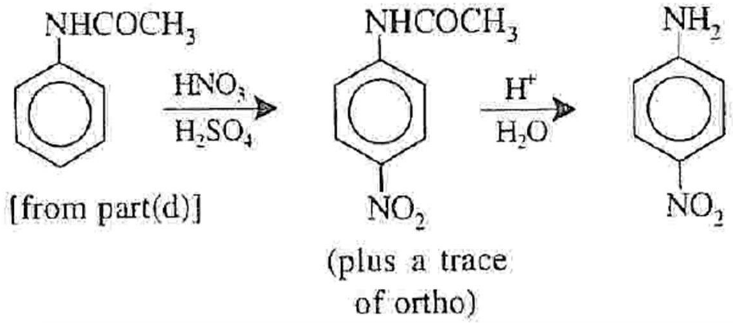


(by nitration of benzene)

(d)

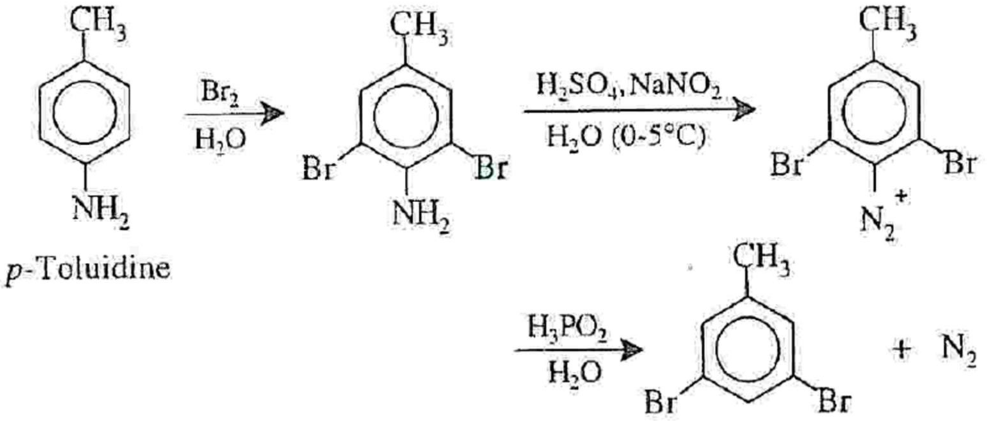


(e)



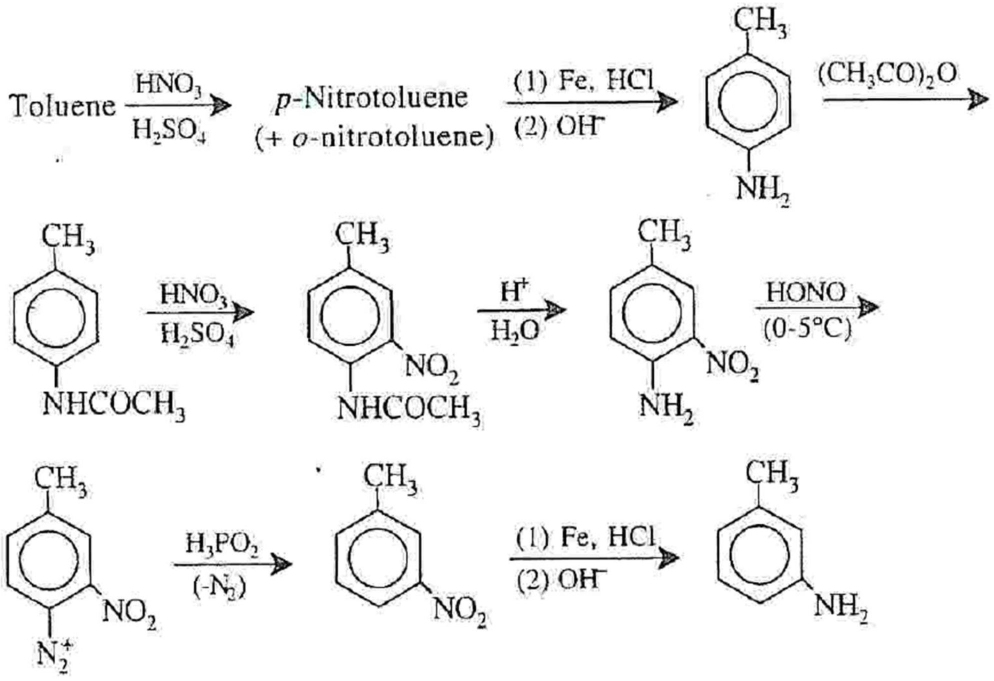
Problem 20.12 ➤ 3,5-Dibromotoluen elde etmek için yukarıdaki tepkime dizisinde nasıl bir değişiklik yapardınız?

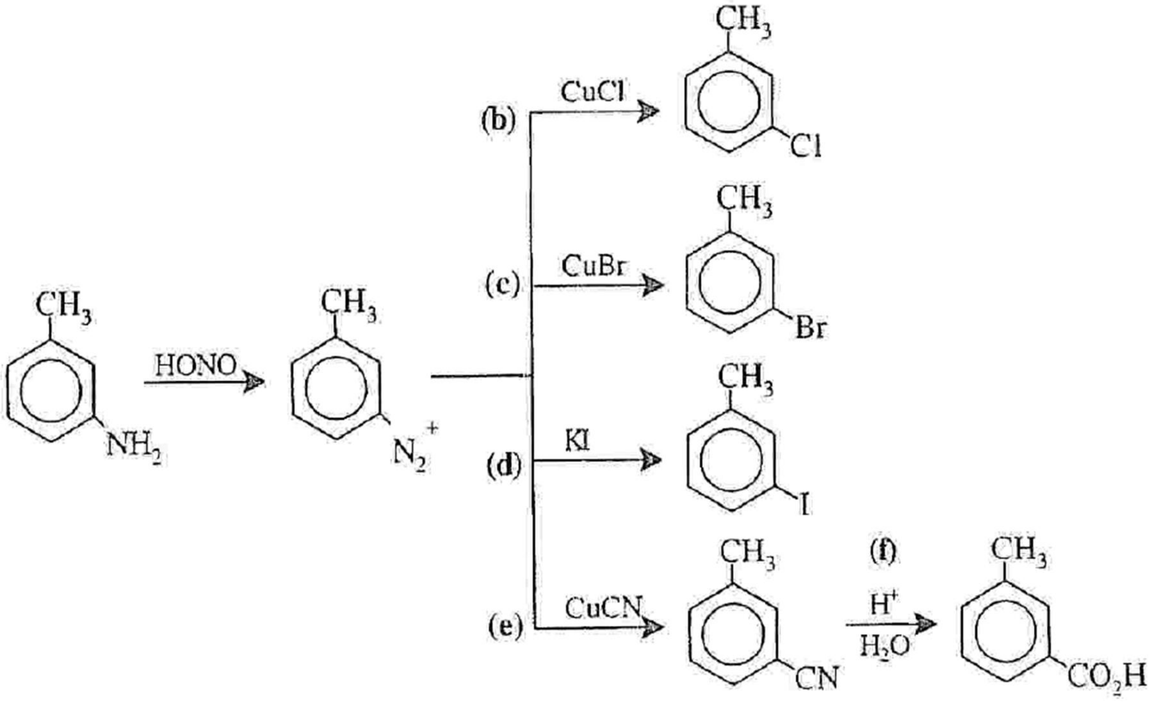
20.12



Problem 20.13 ➤ (a) *m*-Toluidinden çıkarak yapılan *m*-florotoluenin sentezini Altbölüm 20.8D'de gördük. *m*-Toluidini toluenden çıkarak nasıl sentezlersiniz? (b) *m*-Klorotolueni nasıl sentezlersiniz? (c) *m*-Bromotolueni? (d) *m*-İyodotolueni? (e) *m*-Tolunitrili (m-$CH_3C_6H_4CN$)? (f) *m*-Toluik asiti?

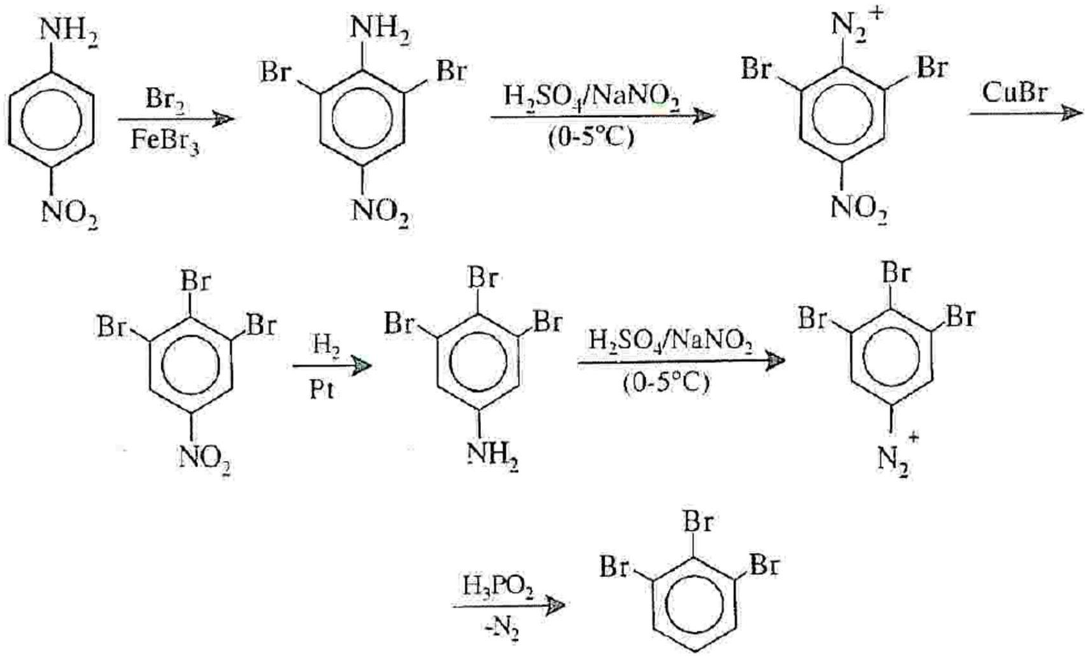
20.13 (a)



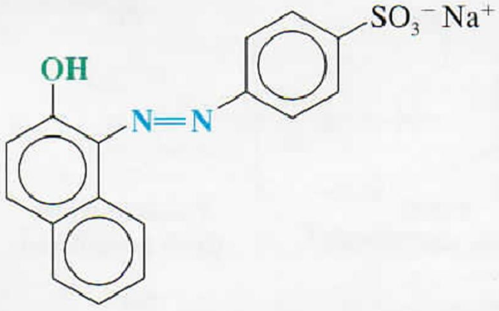


Problem 20.14 ➤ 1,2,3-Tribromobenzeni, *p*-nitroanilinden [Problem 20.11 (e)] çıkarak nasıl sentezleyebilirsiniz?

20.14

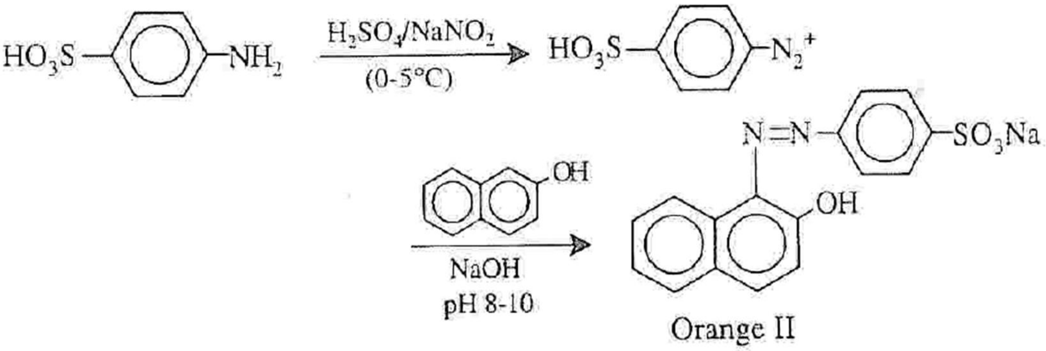


Problem 20.15 ➤ Orange II'nin 2-naftol ve *p*-aminobenzensülfonik asitten sentezini gösteriniz.

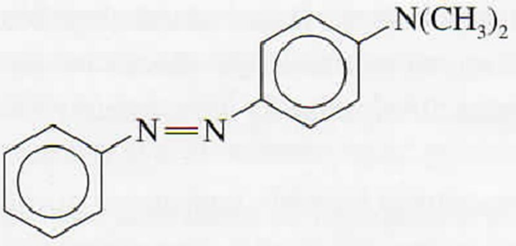


Orange II

20.15

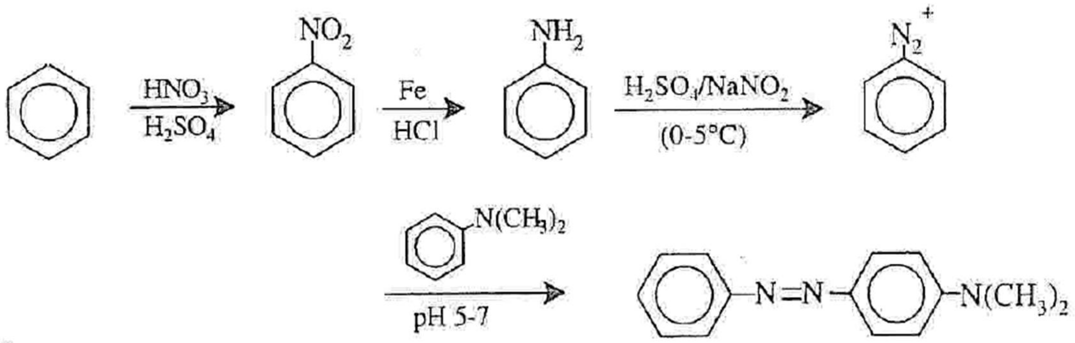


Problem 20.16 ➤ Tereyağ sarısı, bir zamanlar margarinleri renklendirmek amacıyla kullanılmış bir boyadır. Kanserojen olduğu sanıldığından, artık gıdalara katılması yasaklanmıştır. Tereyağ sarısını, benzen ve *N*,*N*-dimetilanilinden çıkarak sentezleyiniz.



Tereyağ sarısı

20.16



Azo bileşikleri, kalay(II) klorür dahil, çeşitli indirgenlerle aminlere indirgenebilirler. **Problem 20.17**

$$Ar—N=N—Ar' \xrightarrow{SnCl_2} ArNH_2 + Ar'NH_2$$

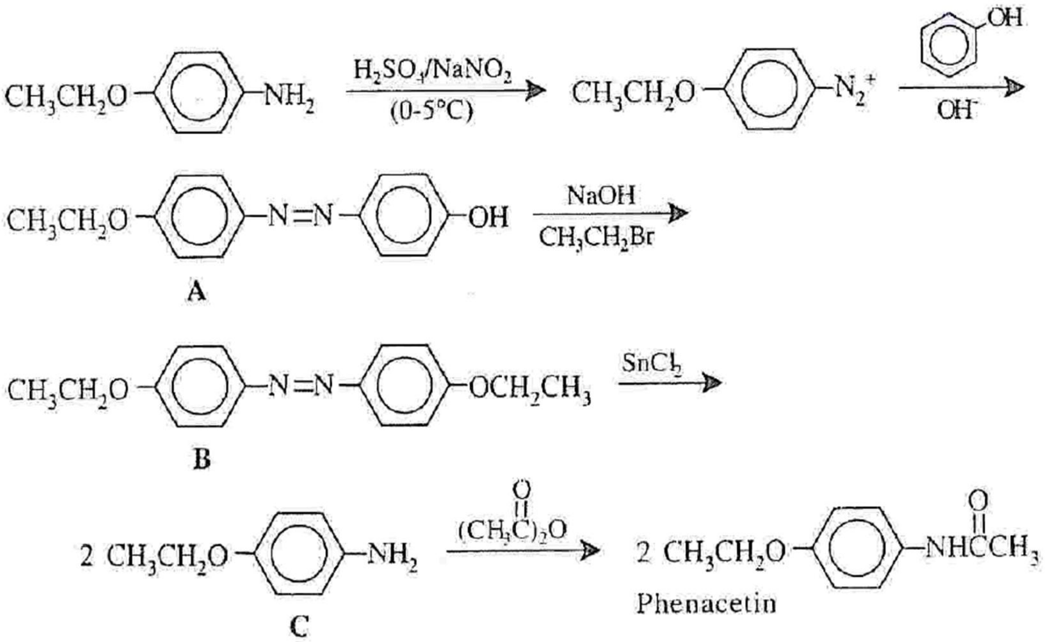
Bu indirgenme, aşağıdaki örnekte görüldüğü gibi, sentezlerde yararlı olabilir:

$$\text{4-Etoksianilin} \xrightarrow[\text{(2) fenol, } OH^-]{\text{(1) HONO } H_3O^+} \textbf{A}\ (C_{14}H_{14}N_2O_2) \xrightarrow{NaOH,\ CH_3CH_2Br} \textbf{B}\ (C_{16}H_{18}N_2O_2) \xrightarrow{SnCl_2}$$

$$\text{iki eşdeğer mol } \textbf{C}\ (C_8H_{11}NO) \xrightarrow{\text{asetik anhidrit}} \text{fenasetin}\quad (C_{10}H_{13}NO_2)$$

Fenasetin ve **A, B, C** ara ürünlerinin yapılarını yazınız. (Eskiden yatıştırıcı olarak kullanılan fenasetin, Problem 18.35'in de konusudur.)

20.17

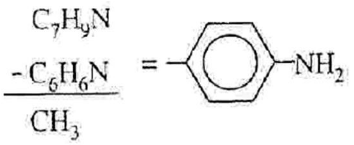


Problem 20.18 ➤ Bir **A** amininin molekül formülü C_7H_9N'dir. Bu amin sulu potasyum hidroksit içerisinde benzensülfonil klorür ile çalkalandığında berrak bir çözelti oluşur. Çözelti asitlendirilirse bir çökelek meydana gelir. **A**, $NaNO_2$ ve HCl ile 0 – 5°C'da tepkimeye sokulur ve sonra 2-naftol ile etkileştirilirse belirgin renkli bir bileşik oluşur. **A** bileşiğinin İR spektrumu 815 cm^{-1} de şiddetli bir band verir. **A** nın yapısı nedir?

20.18 (1) That **A** reacts with benzenesulfonyl chloride in aqueous KOH to give a clear solution, which on acidification yields a precipitate, shows that **A** is a primary amine.

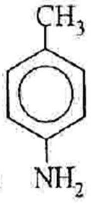
(2) That diazotization of **A** followed by treatment with 2-naphthol gives an intensely colored precipitate shows that **A** is a primary aromatic amine; that is, **A** is a substituted aniline.

(3) Consideration of the molecular formula of **A** leads us to conclude that **A** is a methylaniline (i.e., a toluidine).



But is **A** 2-methylaniline, 3-methylaniline, or 4-methylaniline?

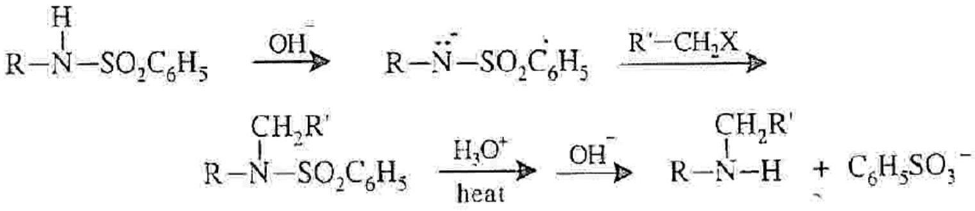
(4) This question is answered by the IR data. A single absorption peak in the 680–840 cm^{-1} region at 815 cm^{-1} is indicative of a para substituted benzene. Thus, **A** is 4-methylaniline (*p*-toluidine).



A

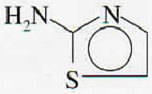
Birincil aminlerin sülfonamitleri *saf* ikincil aminlerin sentezinde sıklıkla kullanılır. Bu sentezin nasıl yapıldığını gösteriniz. ◄ **Problem 20.19**

20.19 First convert the sulfonamide to its anion, then alkylate the anion with an alkyl halide, then remove the $-SO_2C_6H_5$ group by hydrolysis. For example,



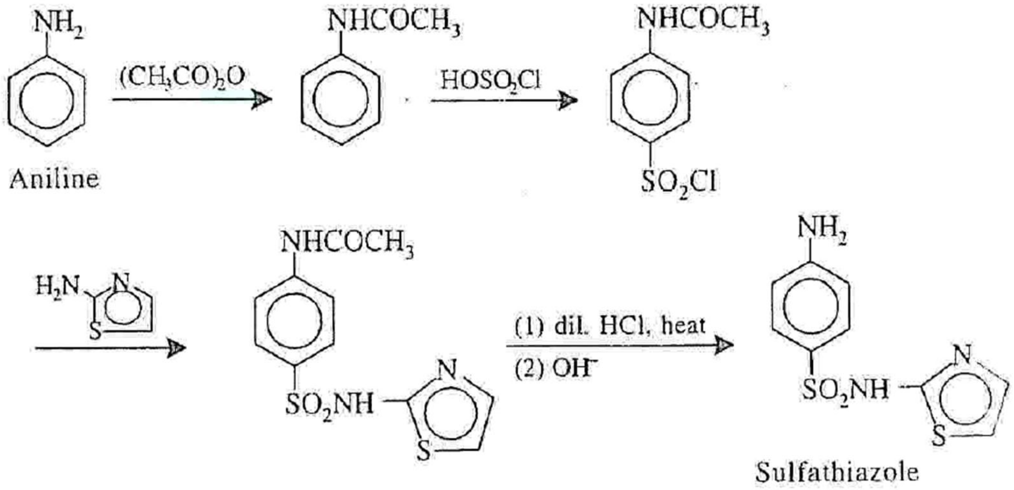
$$R-\overset{H}{N}-SO_2C_6H_5 \xrightarrow{OH^-} R-\ddot{N}^{-}-SO_2C_6H_5 \xrightarrow{R'-CH_2X} R-\overset{CH_2R'}{N}-SO_2C_6H_5 \xrightarrow[heat]{H_3O^+} \xrightarrow{OH^-} R-\overset{CH_2R'}{N}-H + C_6H_5SO_3^-$$

Problem 20.20 ► (a) Anilinden ve 2-aminotiyazolden çıkarak sülfotiyazol sentezleyiniz. (b) Sülfatiyazolü süksinilsülfatiyazole nasıl dönüştürebilirsiniz?

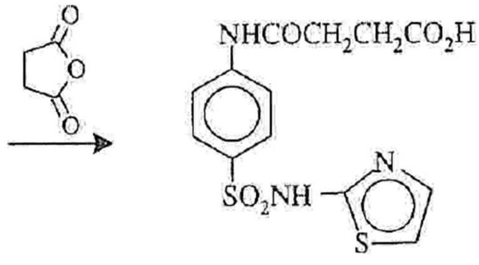


2-Aminotiyazol

20.20 (a)



(b)



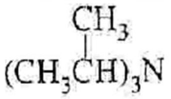
Succinylsulfathiazole

20.21 Aşağıdaki bileşiklerin yapı formüllerini yapınız:

(a) Benzilmetilamin	**(k)** Dimetilaminyum klorür
(b) Triizopropilamin	**(l)** 2-Metilimidazol
(c) *N*-Etil-*N*-metilanilin	**(m)** 3-Amino-1-propanol
(d) *m*-Toluidin	**(n)** Tetrapropilamonyum klorür
(e) 2-Metilpirol	**(o)** Pirolidin
(f) *N*-Etilpiperidin	**(p)** *N*,*N*-Dimetil-*p*-toluidin
(g) *N*-Etilpiridinyum bromür	**(q)** 4-Metoksianilin
(h) 3-Piridinkarboksilik asit	**(r)** Tetrametilamonyum hidroksit
(i) İndol	**(s)** *p*-Aminobenzoik asit
(j) Asetanilit	**(t)** *N*-Metilanilin

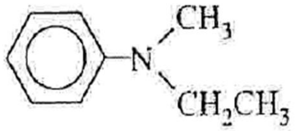
20.21 (a) $C_6H_5CH_2NHCH_3$

(b)

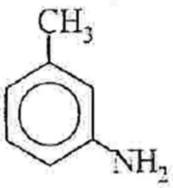


$(CH_3\overset{CH_3}{\overset{|}{C}}H)_3N$

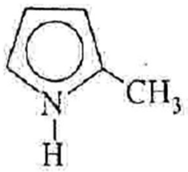
(c)



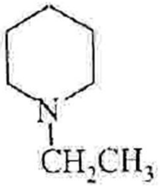
(d)

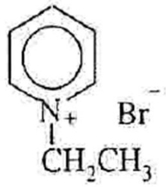


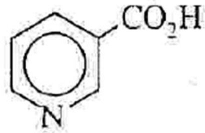
(e)

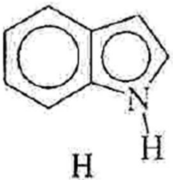


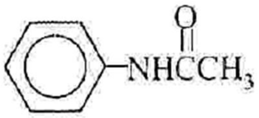
(f)

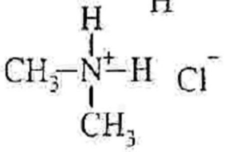


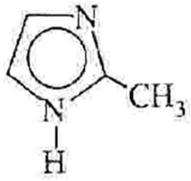
(g) 

(h) 

(i) 

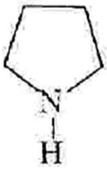
(j) 

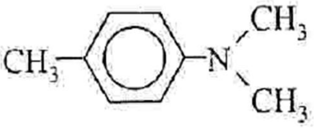
(k) 
$CH_3-\overset{H}{\underset{CH_3}{N^+}}-H\ Cl^-$

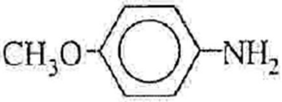
(l) 

(m) $H_2NCH_2CH_2CH_2OH$

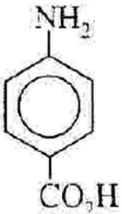
(n) $(CH_3CH_2CH_2)_4N^+\ Cl^-$

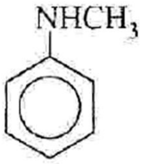
(o) 

(p) 

(q) 

(r) $(CH_3)_4N^+\ OH^-$

(s) 

(t) 

20.22 Aşağıdaki bileşiklerin yaygın adlarını veya sistematik adlarını yazınız:

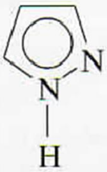
(a) $CH_3CH_2CH_2NH_2$

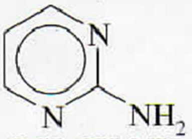
(b) $C_6H_5NHCH_3$

(c) $(CH_3)_2CH\overset{+}{N}(CH_3)_3\ I^-$

(d) *o*-$CH_3C_6H_4NH_2$

(e) *o*-$CH_3OC_6H_4NH_2$

(f) 

(g) 

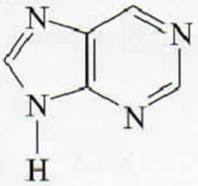
(h) $C_6H_5CH_2NH_3^+Cl^-$

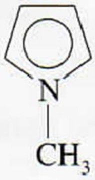
(i) $C_6H_5N(CH_2CH_2CH_3)_2$

(j) $C_6H_5SO_2NH_2$

(k) $CH_3NH_3^+CH_3CO_2^-$

(l) $HOCH_2CH_2CH_2NH_2$

(m) 

(n) 

20.22 (a) Propylamine

(b) *N*-Methylaniline

(c) Isopropyltrimethylammonium iodide

(d) 2-Methylaniline (*o*-toluidine)

(e) 2-Methoxyaniline (or *o*-methoxyaniline)

(f) Pyrazole

(g) 2-Aminopyrimidine

(h) Benzylaminium chloride

(i) *N*,*N*-Dipropylaniline

(j) Benzenesulfonamide

(k) Methylaminium acetate

(l) 3-Amino-1-propanol

(m) Purine

(n) *N*-Methylpyrrole

20.23 Aşağıdaki bileşiklerin her birinden benzilamini nasıl sentezlersiniz?

(a) Benzonitril

(b) Benzamit

(c) Benzil bromür (iki yol)

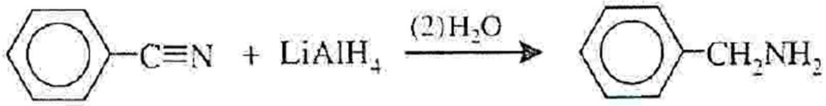
(d) Benzil tosilat

(e) Benzaldehit

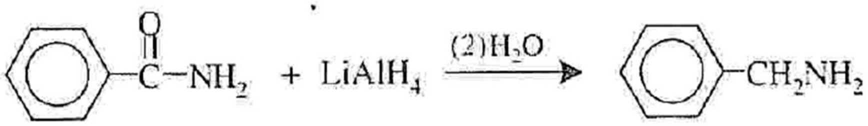
(f) Fenilnitrometan

(g) Fenilasetamit

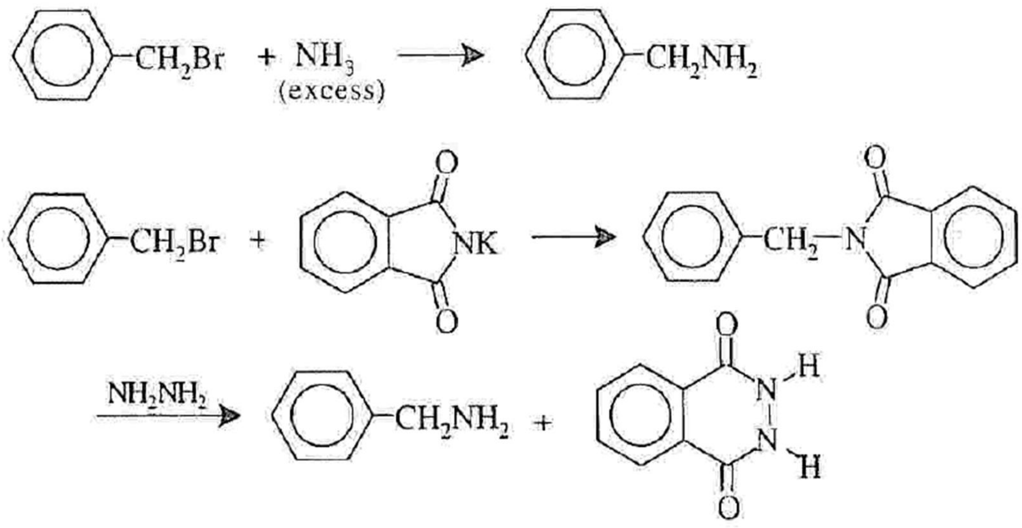
20.23 (a)



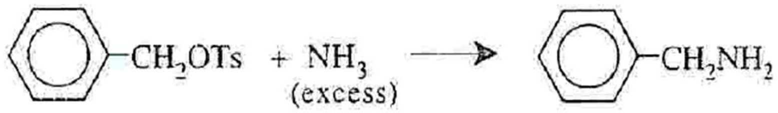
(b)



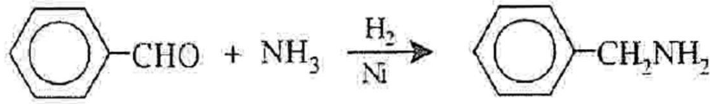
(c)



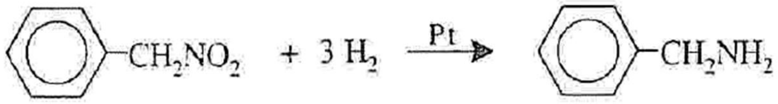
(d)



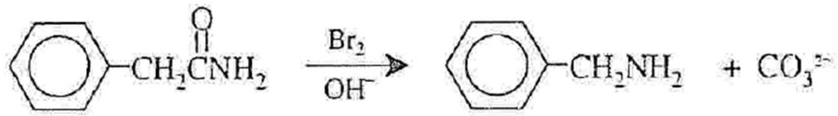
(e)



(f)



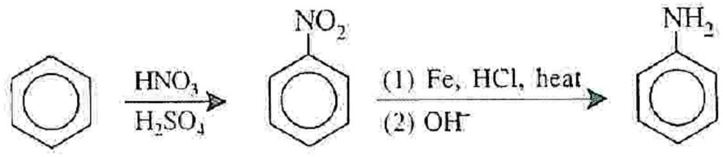
(g)



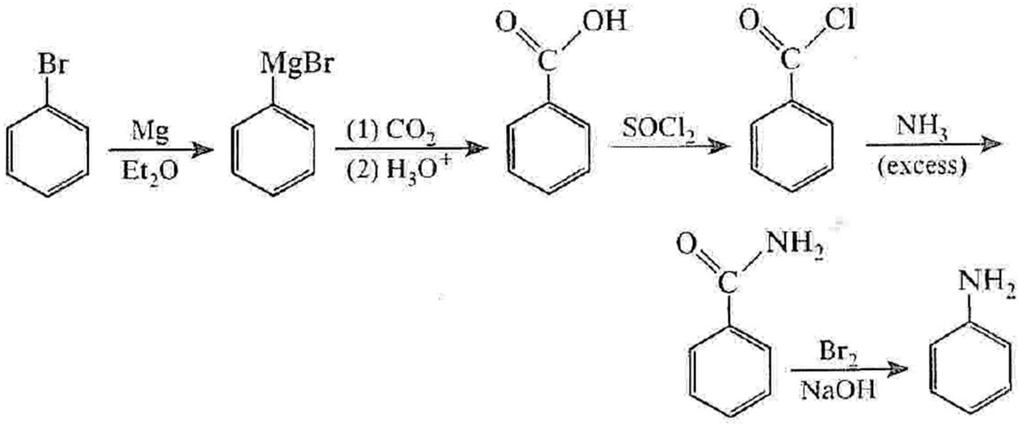
20.24 Aşağıdaki bileşiklerin her birinden anilini sentezleyiniz.

(a) Benzen **(b)** Bromobenzen **(c)** Benzamit

20.24 (a)

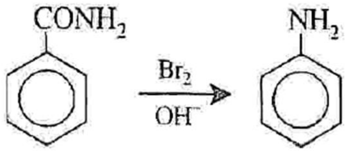


(b)



Hofmann rearrangement

(c)



20.25 Aşağıdaki bileşikleri bütil alkolden çıkarak sentezleyiniz.

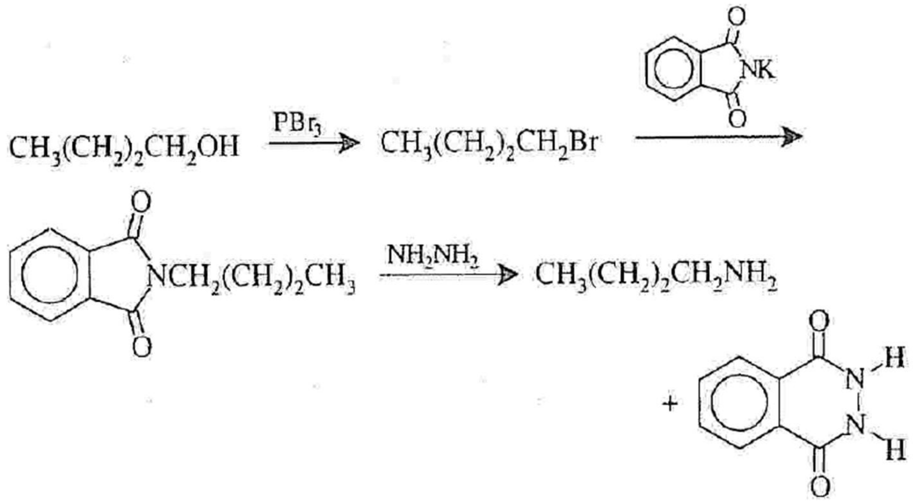
(a) Bütilamin (2° ve 3° amin içermeyecek)

(b) Pentilamin

(c) Propilamin

(d) Bütilmetilamin

20.25 (a)



(b) $CH_3(CH_2)_2CH_2Br \xrightarrow{NaCN} CH_3(CH_2)_3CN \xrightarrow[(2)\,H_2O]{(1)\,LiAlH_4,\ Et_2O} CH_3(CH_2)_3CH_2NH_2$

[from part(a)]

(c) $CH_3(CH_2)_2CH_2OH \xrightarrow[(2)\,H^+]{(1)\,KMnO_4,\ OH^-} CH_3CH_2CH_2CO_2H$

$\xrightarrow[(2)\,NH_3]{(1)\,SOCl_2} CH_3CH_2CH_2CONH_2 \xrightarrow[OH^-]{Br_2} CH_3CH_2CH_2NH_2$

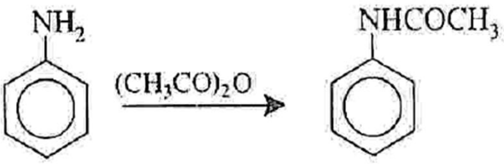
(d) $CH_3(CH_2)_2CH_2OH \xrightarrow[CH_2Cl_2]{PCC} CH_3CH_2CH_2CHO \xrightarrow[H_2,\ Ni]{CH_3NH_2}$

$CH_3CH_2CH_2CH_2NHCH_3$

20.26 Anilini aşağıdaki bileşiklerin her birine nasıl dönüştürürsünüz? (Problemin önceki şıklarında elde ettiğinizi yeniden elde etmenize gerek yoktur.)

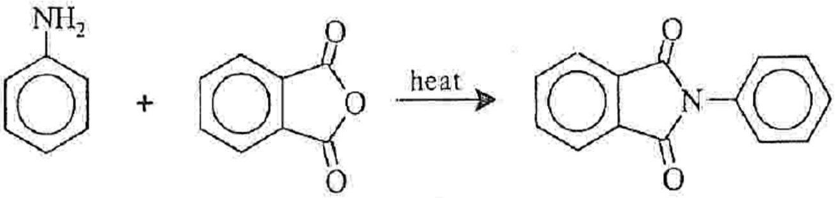
(a) Asetanilit
(b) *N*-Fenilftalimit
(c) *p*-Nitroanilin
(d) Sülfanilamit
(e) *N,N*-Dimetilanilin
(f) Florobenzen
(g) Klorobenzen
(h) Bromobenzen
(i) İyodobenzen
(j) Benzonitril
(k) Benzoik asit
(l) Fenol
(m) Benzen
(n) *p*-(Fenilazo)fenol
(o) *N,N*-Dimetil-*p*-(fenilazo)anilin

20.26 (a)



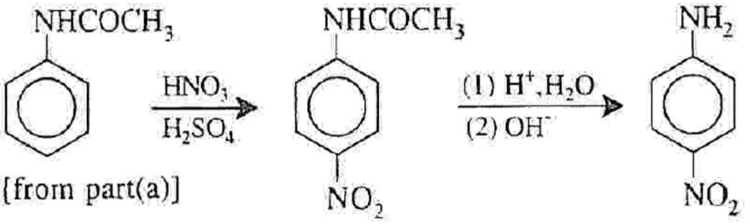
NH$_2$
(CH$_3$CO)$_2$O
NHCOCH$_3$

(b)



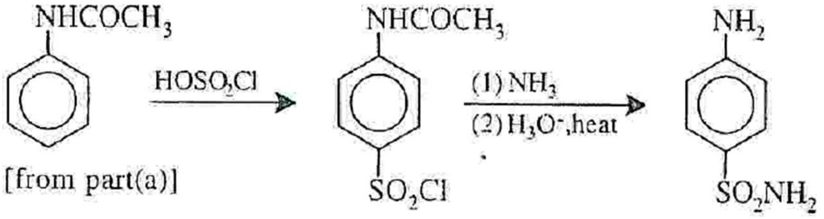
NH$_2$
+
O
O
O
heat
O
N
O

(c)



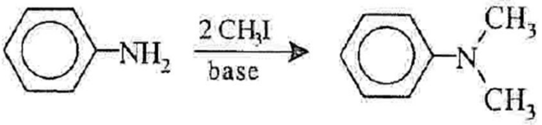
NHCOCH$_3$
HNO$_3$
H$_2$SO$_4$
NHCOCH$_3$
NO$_2$
(1) H$^+$,H$_2$O
(2) OH$^-$
NH$_2$
NO$_2$
[from part(a)]

(d)

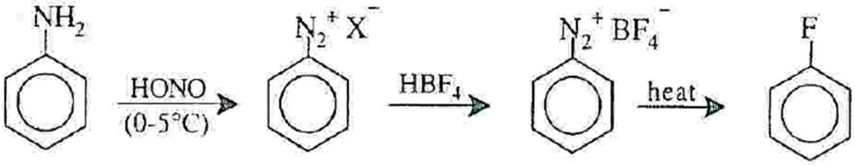


[from part(a)]

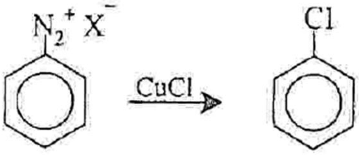
(e)



(f)

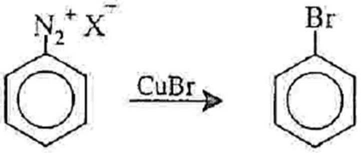


(g)



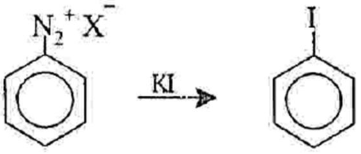
[from part(f)]

(h)



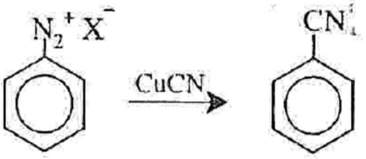
[from part(f)]

(i)

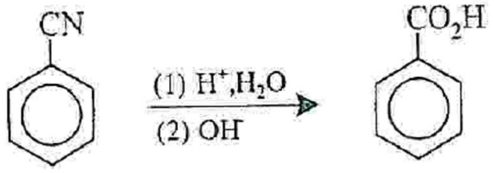


[from part(f)]

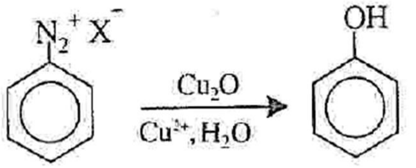
(j)



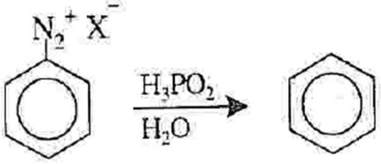
[from part(f)]

(k) 

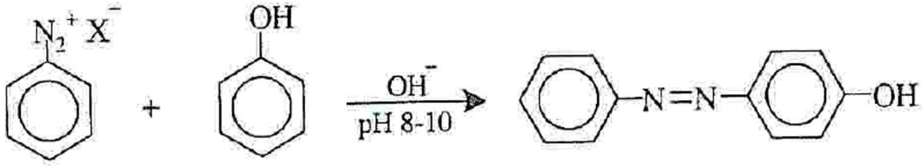
[from part(j)]

(l) 

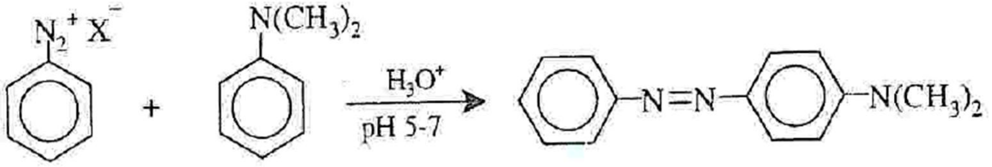
[from part(f)]

(m) 

[from part(f)]

(n) 

[from part(f)] [from part(l)]

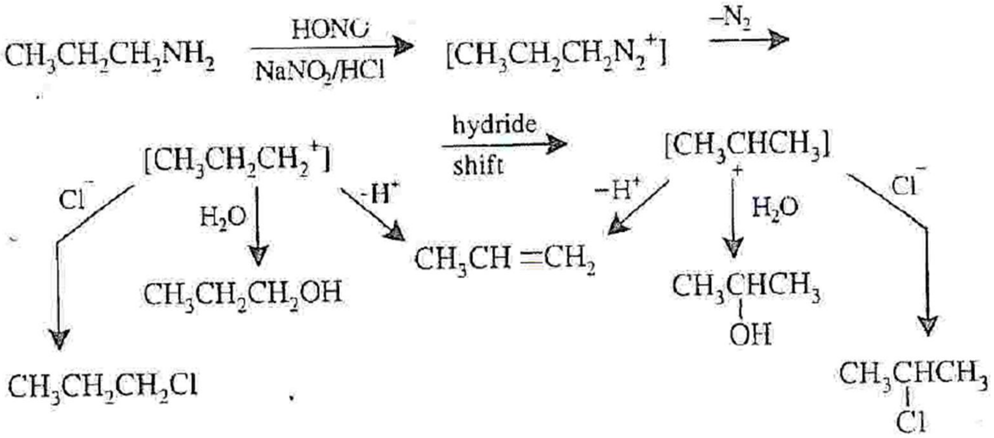
(o) 

[from part(f)] [from part(e)]

20.27 Aşağıdaki aminlerin herbiri sulu sodyum nitrit ve hidroklorik asitle tepkimeye girdiğinde hangi ürünlerin oluşmasını beklersiniz?

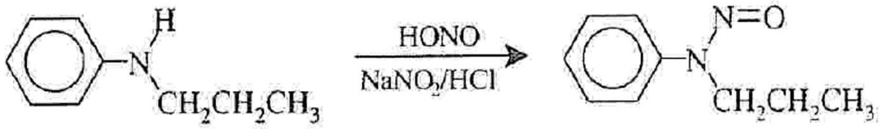
(a) Propilamin
(b) Dipropilamin
(c) *N*-Propilanilin
(d) *N*,*N*-Dipropilanilin
(e) *p*-Propilanilin

20.27 (a)

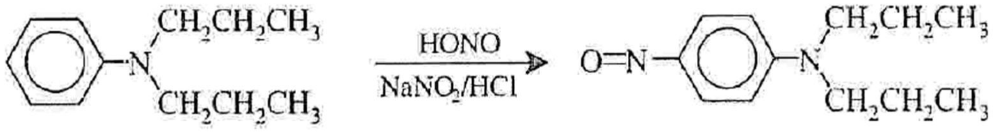


(b) $$(CH_3CH_2CH_2)_2NH \xrightarrow[NaNO_2/HCl]{HONO} (CH_3CH_2CH_2)_2N-N{=}O$$

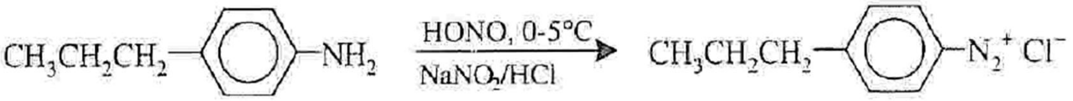
(c)



(d)



(e)



20.28 **(a)** Bir önceki problemde verilen aminlerin her biri benzensülfonil klorür ve sulu potusyum hidroksitin aşırısıyla tepkimeye girerse hangi ürünler oluşur? **(b)** Her bir tepkimede neler gözlemeyi beklersiniz? **(c)** Tepkime sonunda çözeltiye ya da karışıma asit eklerseniz neler gözlersiniz?

20.28 (a) $$CH_3CH_2CH_2NH_2 + C_6H_5SO_2Cl \xrightarrow[H_2O]{KOH} CH_3CH_2CH_2\overset{-}{N}SO_2C_6H_5\ K^+$$

Clear solution

$$\xrightarrow{H_3O^+} CH_3CH_2CH_2NHSO_2C_6H_5$$

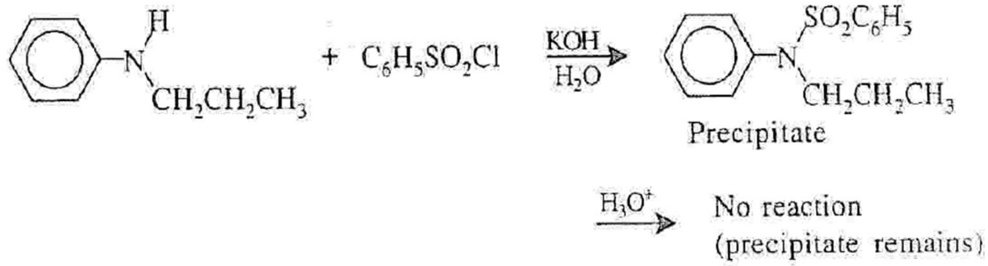
Precipitate

(b) $$(CH_3CH_2CH_2)_2NH + C_6H_5SO_2Cl \xrightarrow[H_2O]{KOH} (CH_3CH_2CH_2)_2NSO_2C_6H_5$$

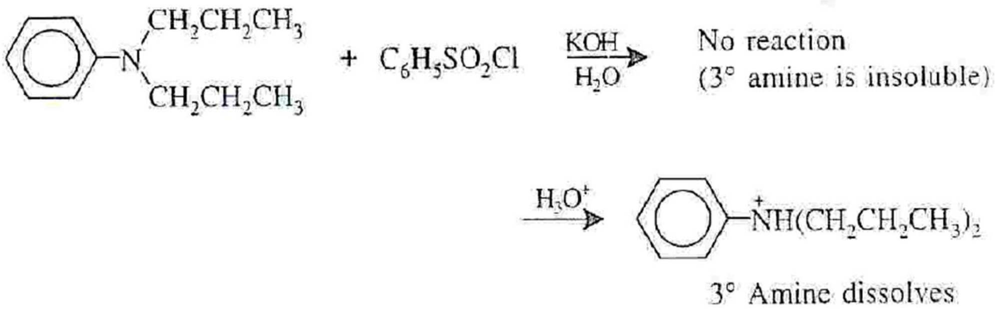
Precipitate

$\xrightarrow{H_3O^+}$ No reaction (precipitate remains)

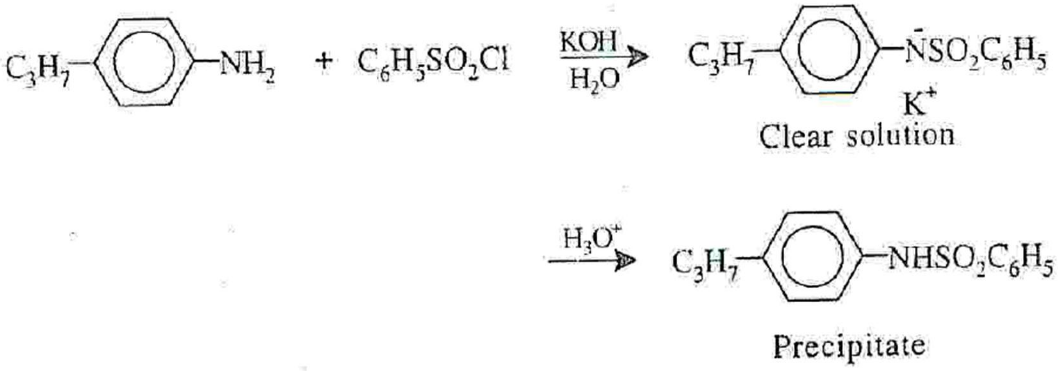
(c)



(d)

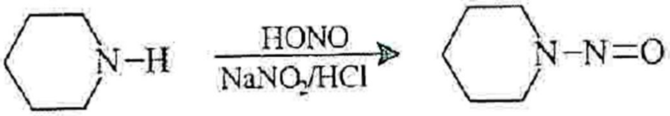


(e)

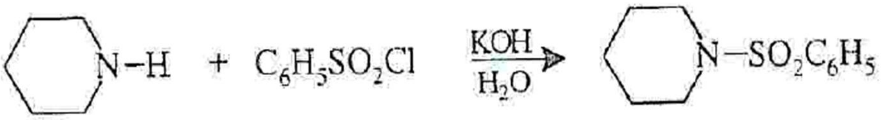


20.29 (**a**) Piperidinin sulu sodyum nitrit ve hidroklorik asitle tepkimesinden hangi ürün oluşur? (**b**) Piperidinin benzensülfonil klorür ve sulu potasyum hidroksitin aşırısıyla vereceği ürün nedir?

20.29 (a)



(b)



20.30 Aşağıdaki tepkimelerin ürünlerini yazınız:

(a) Etilamin + benzoil klorür ⟶

(b) Metilamin + asetik anhidrit ⟶

(c) Metilamin + süksinik anhidrit ⟶

(d) (c)'nin ürünü $\xrightarrow{\text{ısı}}$

(e) Pirolidin + ftalik anhidrit ⟶

(f) Pirol + asetik anhidrit ⟶

(g) Anilin + propanoil klorür ⟶

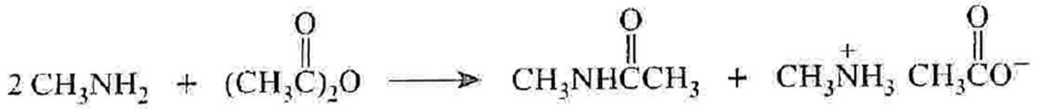
(h) Tetraetilammonyum hidroksit $\xrightarrow{\text{ısı}}$

(i) *m*-Dinitrobenzen + $H_2S \xrightarrow[C_2H_5OH]{NH_3}$

(j) *p*-Toluidin + Br_2 (aşırı) $\xrightarrow[H_2O]{}$

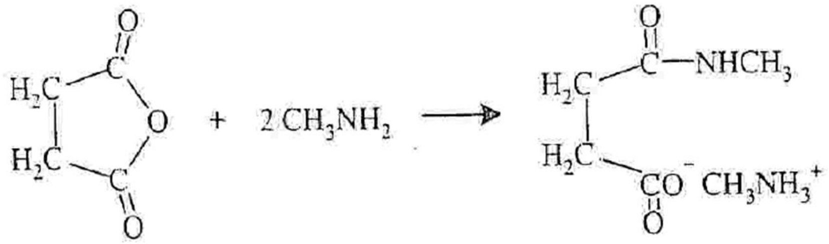
20.30 (a) $2\,CH_3CH_2NH_2 + C_6H_5COCl \longrightarrow CH_3CH_2NHCOC_6H_5 + CH_3CH_2NH_3^+\,Cl^-$

(b)

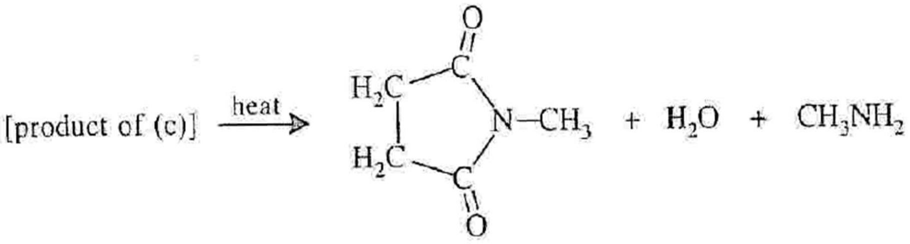


$$2\,CH_3NH_2 + (CH_3\overset{O}{\overset{\|}{C}})_2O \longrightarrow CH_3NH\overset{O}{\overset{\|}{C}}CH_3 + CH_3\overset{+}{N}H_3\ CH_3\overset{O}{\overset{\|}{C}}O^-$$

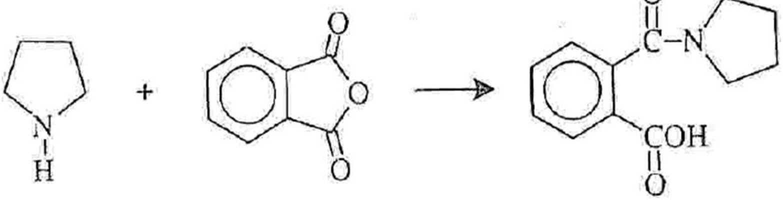
(c)



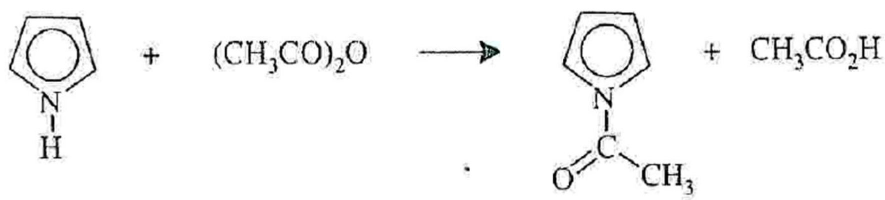
(d)



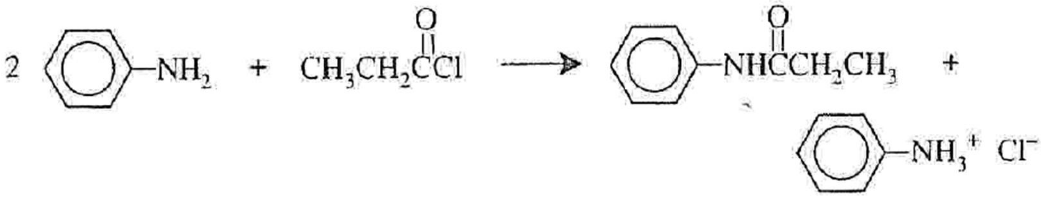
(e)



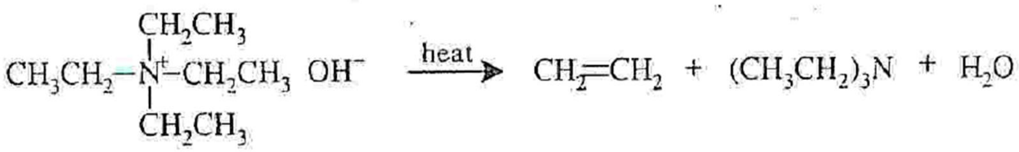
(f)



(g)

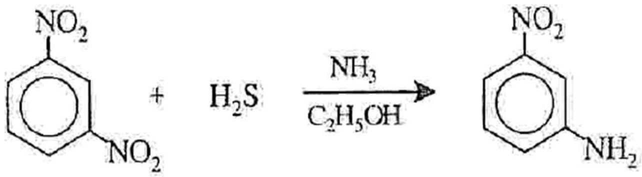


(h)

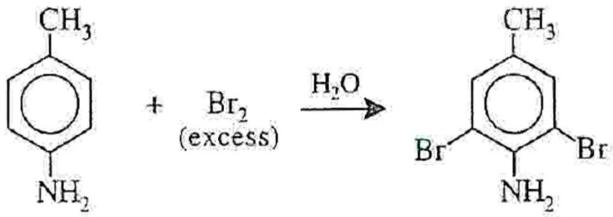


$$CH_3CH_2-\overset{CH_2CH_3}{\underset{CH_2CH_3}{N^+}}-CH_2CH_3\ OH^- \xrightarrow{heat} CH_2{=}CH_2 + (CH_3CH_2)_3N + H_2O$$

(i)



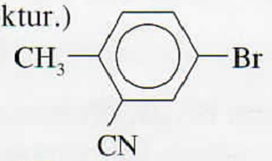
(j)



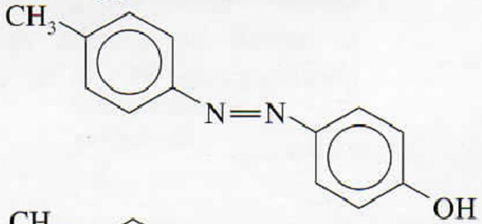
20.31 Aşağıdaki bileşikleri benzen ya da toluenden çıkarak, diazonyum tuzları üzerinden sentezleyiniz. (Problemin önceki basamaklarında elde ettiğiniz bir bileşiği yeniden sentezlemenize gerek yoktur.)

- **(a)** *p*-Florotoluen
- **(b)** *o*-İyodotoluen
- **(c)** *p*-Krozol
- **(d)** *m*-Diklorobenzen
- **(e)** *m*-$C_6H_4(CN)_2$
- **(f)** *m*-İyodofenol
- **(g)** *m*-Bromobenzonitril
- **(h)** 1,3-Dibromo-5-nitrobenzen
- **(i)** 3,5-Dibromoanilin
- **(j)** 3,4,5-Tribromofenol
- **(k)** 3,4,5-Tribromobenzonitril
- **(l)** 2,6-Dibromobenzoik asit
- **(m)** 1,3-Dibromo-2-iyodobenzen
- **(n)** 4-Bromo-2-nitrotoluen
- **(o)** 4-Metil-3-nitrofenol

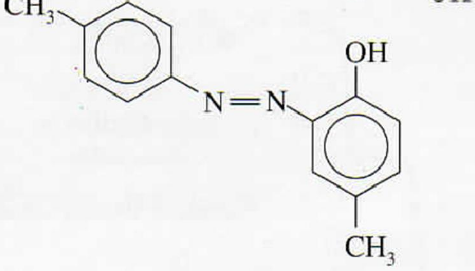
(p)



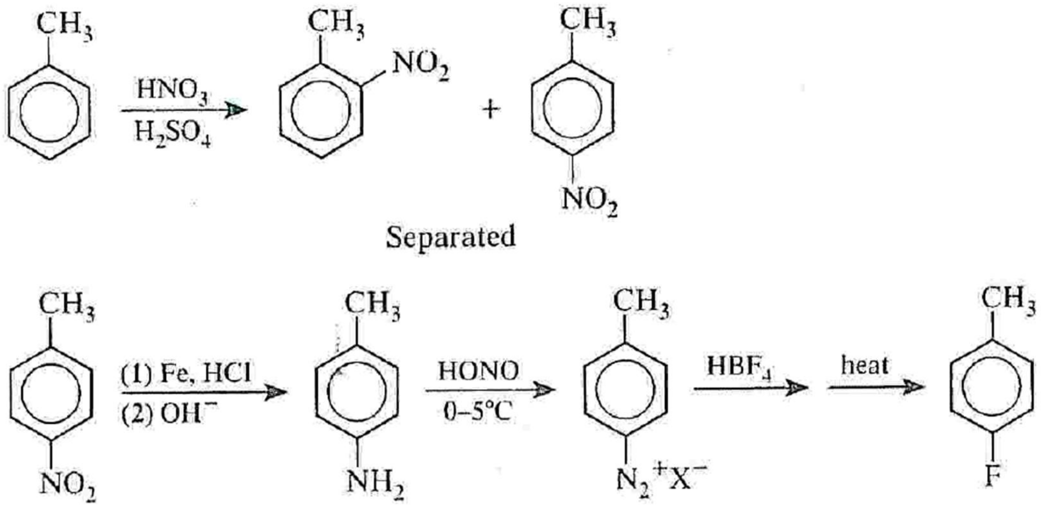
(q)

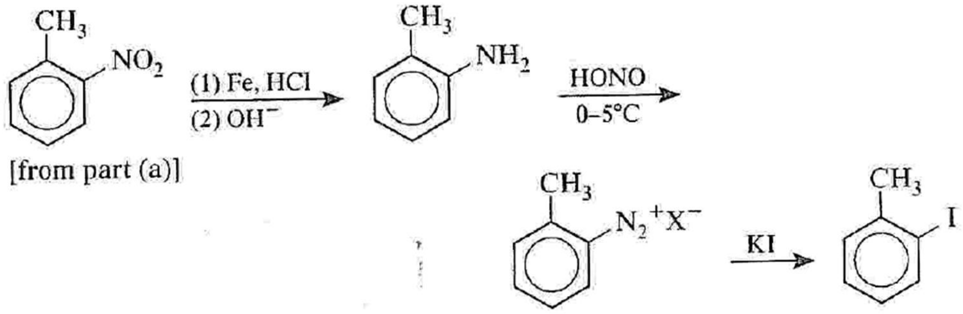


(r)

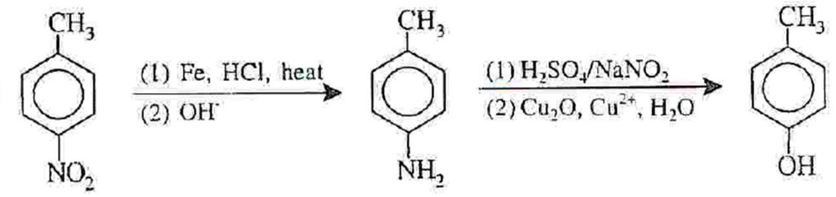


20.31 (a)

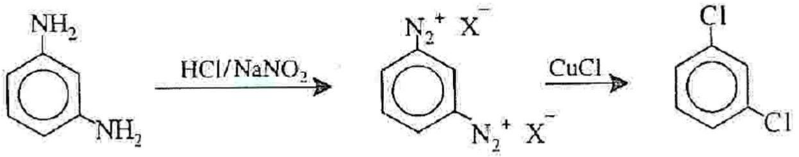

CH3
HNO3
H2SO4
NO2
+
Separated
(1) Fe, HCl
(2) OH−
NH2
HONO
0–5°C
N2+X−
HBF4
heat
F

(b) 

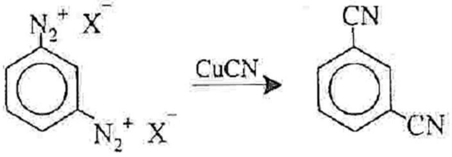
[from part (a)]

(c) 

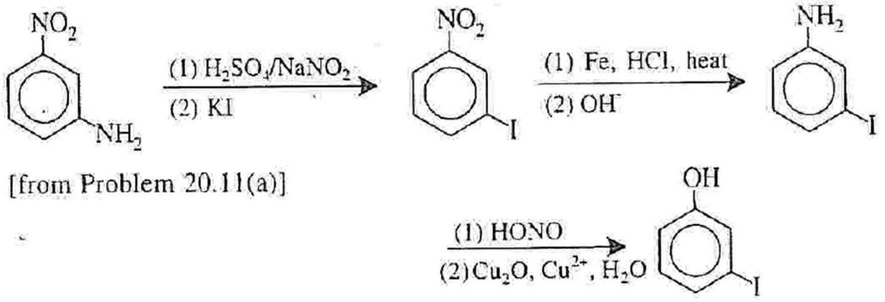
[from part (a)]

(d) 

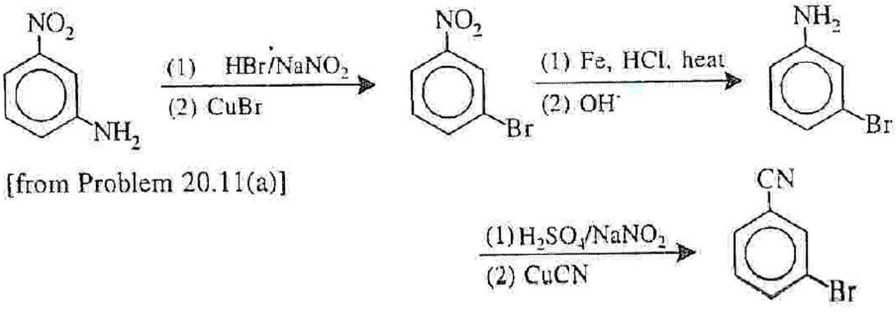
[by reduction of *m*-dinitrobenzene, cf. Problem 20.11(a)]

(e) 

[from part (d)]

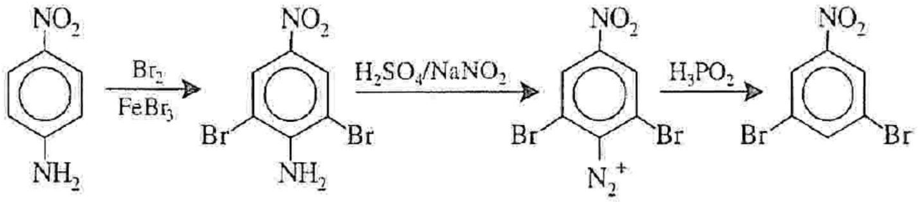
(f) 

[from Problem 20.11(a)]

(g) 

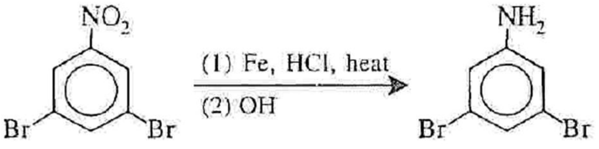
[from Problem 20.11(a)]

(h)



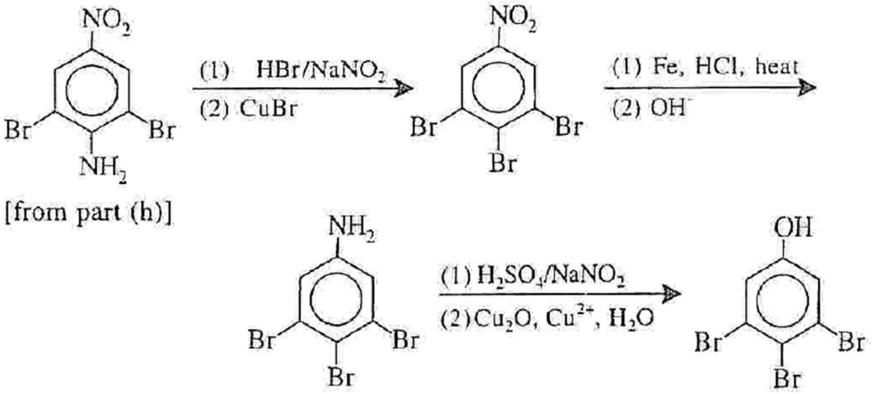
[from Problem 20.11(e)]

(i)



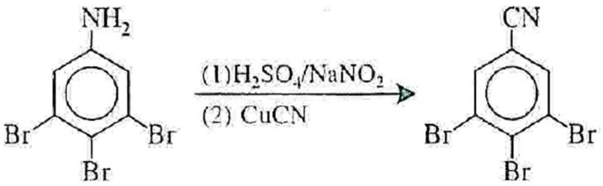
[from part (h)]

(j)



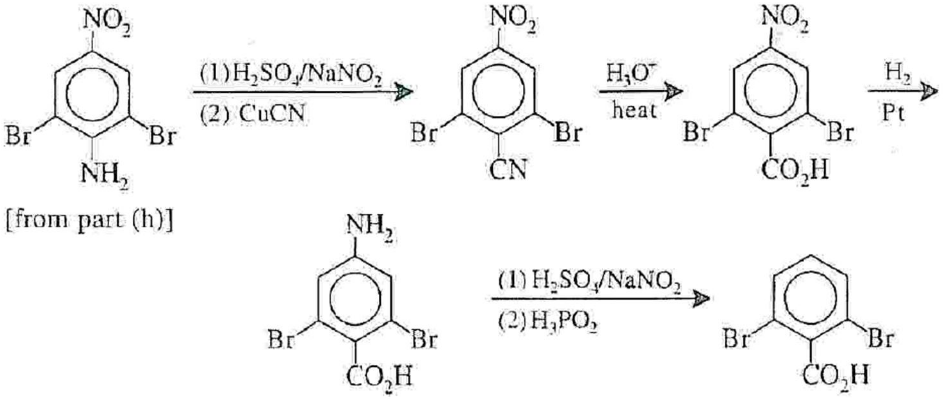
[from part (h)]

(k)



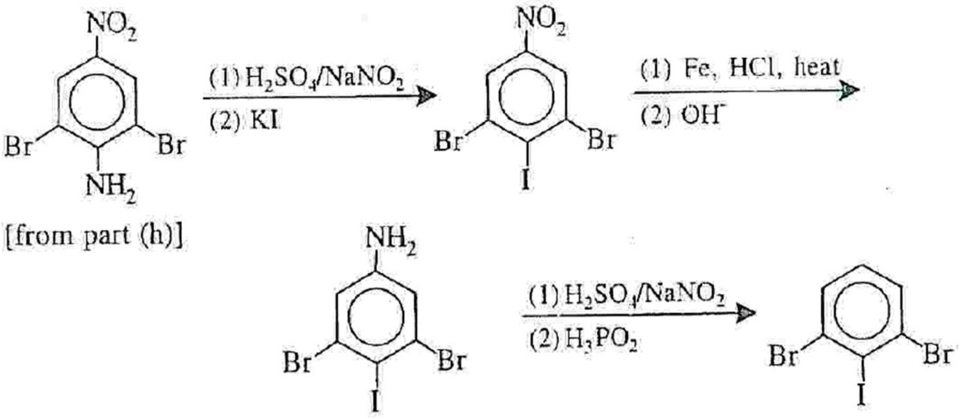
[from part (j)]

(l)



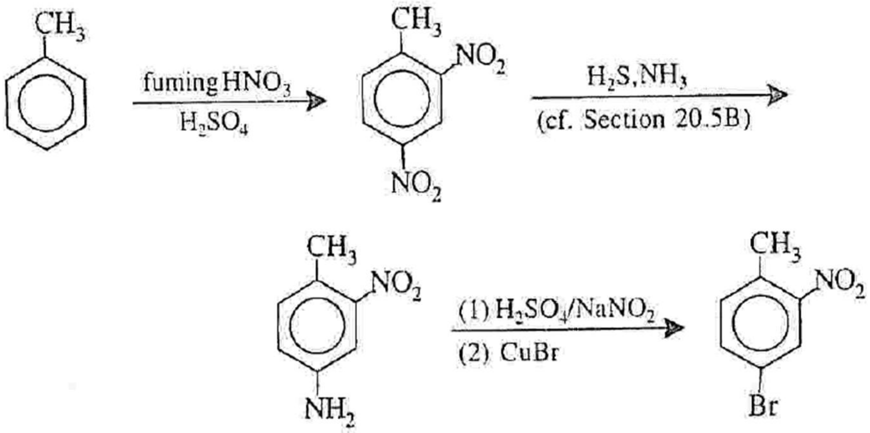
[from part (h)]

(m)

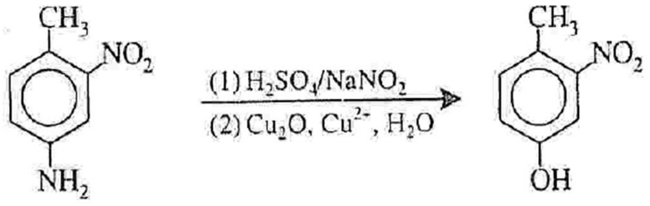


[from part (h)]

(n)

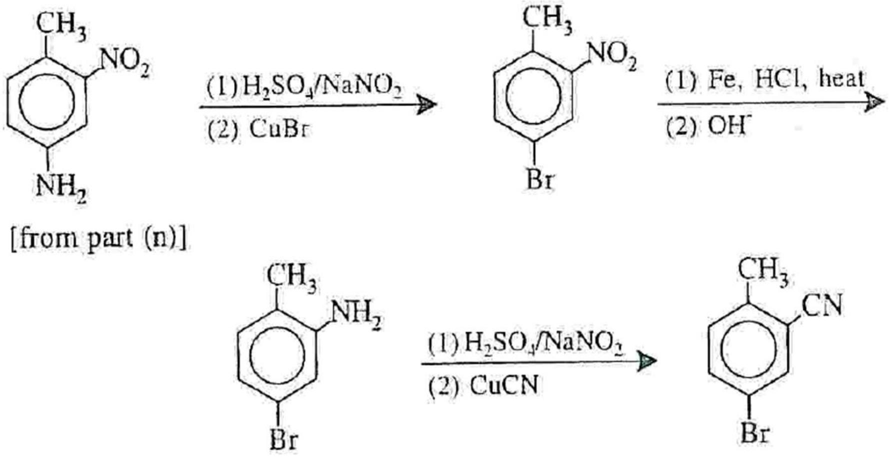


(o)



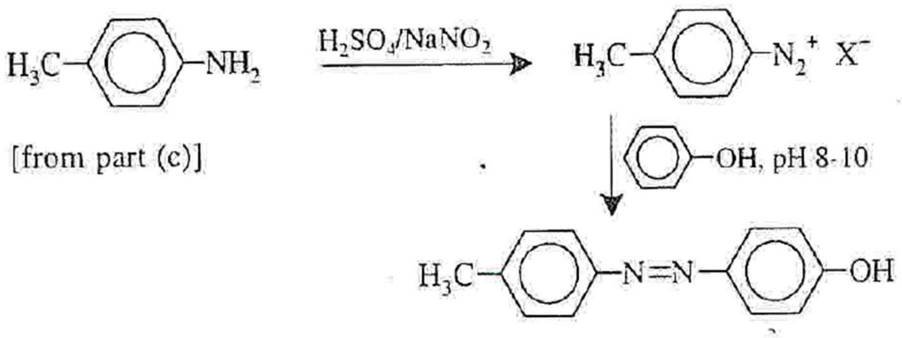
[from part (n)]

(p)

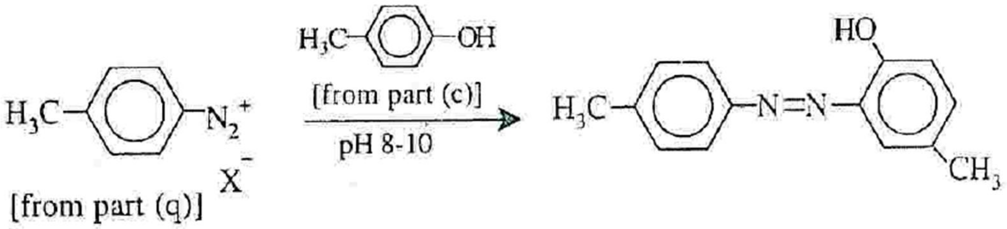


[from part (n)]

(q)



(r)



20.32 Aşağıdaki bileşikleri birbirinden ayırt etmek için basit kimyasal tepkimeler yazınız.

(a) Benzilamin ve benzamit
(b) Allilamin ve propilamin
(c) *p*-Toluidin ve *N*-metilanilin
(d) Sikloheksilamin ve piperidin
(e) Piridin ve benzen
(f) Sikloheksilamin ve anilin
(g) Trietilamin ve dietilamin
(h) Tripropilaminyum klorür ve tetrapropilamonyum klorür
(i) Tetrapropilamonyum klorür ve tetrapropilamonyum hidroksit

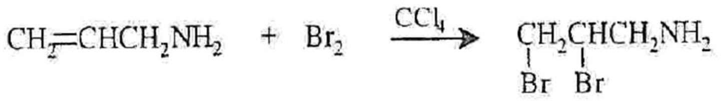
20.32 (a) Benzylamine dissolves in dilute HCl at room temperature,

$$C_6H_5CH_2NH_2 \ + \ H_3O^+ \ + \ Cl^- \xrightarrow{25°C} C_6H_5CH_2\overset{+}{N}H_3\ Cl^-$$

benzamide does not dissolve:

$$C_6H_5CONH_2 \ + \ H_3O^+ \ + \ Cl^- \xrightarrow{25°C} \text{No reaction}$$

(b) Allylamine reacts with (and decolorizes) bromine in carbon tetrachloride instantly.

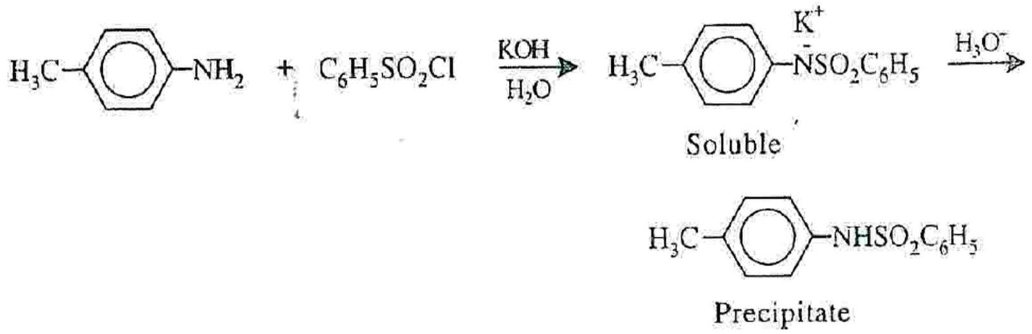


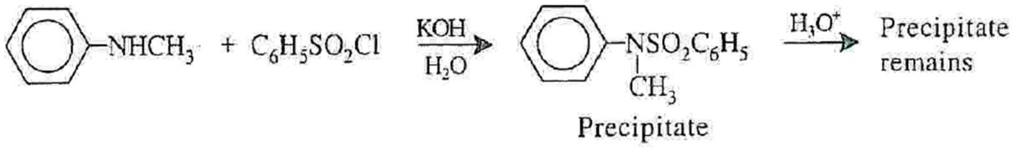
$$CH_2{=}CHCH_2NH_2 \ + \ Br_2 \xrightarrow{CCl_4} \underset{Br}{CH_2}\underset{Br}{CH}CH_2NH_2$$

propylamine does not:

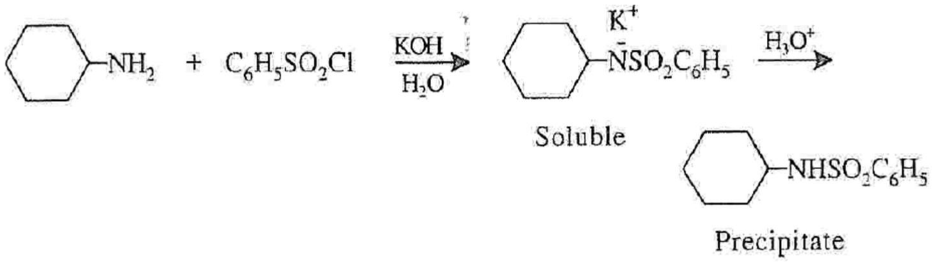
$$CH_3CH_2CH_2NH_2 \ + \ Br_2 \xrightarrow{CCl_4} \begin{array}{l}\text{No reaction if the mixture}\\ \text{is not heated or irradiated}\end{array}$$

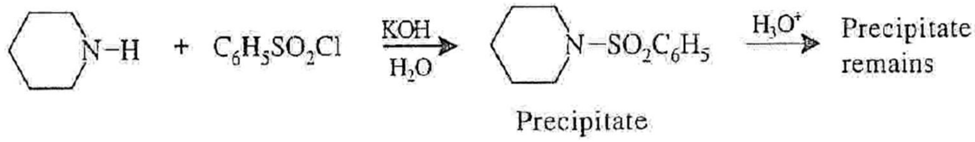
(c) The Hinsberg test:



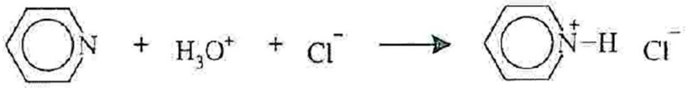


(d) The Hinsberg test:

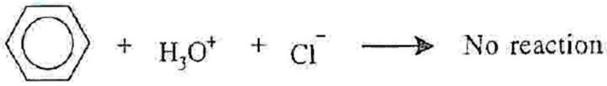




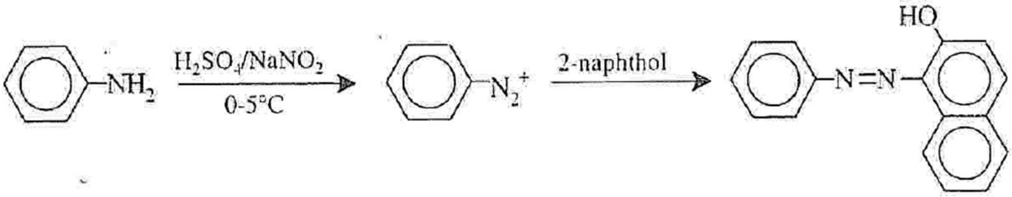
(e) Pyridine dissolves in dilute HCl,



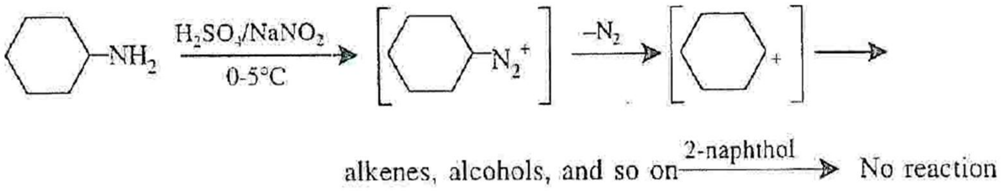
benzene does not:



(f) Aniline reacts with nitrous acid at 0-5°C to give a stable diazonium salt that couples with 2-naphthol, yielding an intensely colored azo compound.



Cyclohexylamine reacts with nitrous acid at 0-5°C to yield a highly unstable diazonium salt—one that decomposes so rapidly that the addition of 2-naphthol gives no azo compound.



(g) The Hinsberg test:

$$(C_2H_5)_3N \; + \; C_6H_5SO_2Cl \xrightarrow[H_2O]{KOH} \text{No reaction} \xrightarrow{H_3O^+} \underset{\text{Soluble}}{(C_2H_5)_3\overset{+}{N}H}$$

$$(C_2H_5)_2NH \; + \; C_6H_5SO_2Cl \xrightarrow[H_2O]{KOH} \underset{\text{Precipitate}}{(C_2H_5)_2NSO_2C_6H_5} \xrightarrow{H_3O^+} \text{Precipitate remains}$$

(h) Tripropylaminium chloride reacts with aqueous NaOH to give a water insoluble tertiary amine.

$$\underset{\text{Water soluble}}{(CH_3CH_2CH_2)_3NH^+ \; Cl^-} \xrightarrow[H_2O]{NaOH} \underset{\text{Water insoluble}}{(CH_3CH_2CH_2)_3N}$$

Tetrapropylammonium chloride does not react with aqueous NaOH (at room temperature), and the tetrapropylammonium ion remains in solution.

$$\underset{\text{Water soluble}}{(CH_3CH_2CH_2)_4N^+ \; Cl^-} \xrightarrow[H_2O]{NaOH} \underset{\text{Water soluble}}{(CH_3CH_2CH_2)_4N^+ \; [Cl^- \text{ or } OH^-]}$$

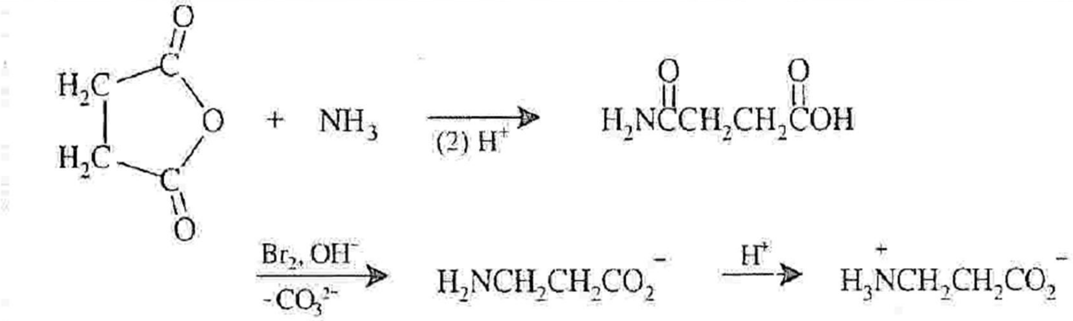
(i) Tetrapropylammonium chloride dissolves in water to give a neutral solution. Tetrapropylammonium hydroxide dissolves in water to give a strongly basic solution.

20.33 Anilin, *p*-kresol, benzoik asit ve toluen karışımını labaratuvarda kullandığınız basit reaktiflerle nasıl ayırabileceğinizi denklemlerle belirtiniz.

20.33 Follow the procedure outlined in the answer to Problem 20.2. Toluene will show the same solubility behavior as benzene.

20.34 β-Aminopropiyonik asidi ($H_3\overset{+}{N}CH_2CH_2CO_2^-$) süksinik anhidritten çıkarak nasıl sentezlersiniz? (β-Aminopropiyonik asit pantotenik asit sentezinde kullanılır; bakınız Problem 18.34.)

20.34



$$+\; NH_3 \xrightarrow{(2)\,H^+} H_2N\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}OH \xrightarrow[-CO_3^{2-}]{Br_2,\, OH^-} H_2NCH_2CH_2CO_2^- \xrightarrow{H^+} H_3\overset{+}{N}CH_2CH_2CO_2^-$$

20.35 Aşağıdaki bileşiklerin her birini belirtilen bileşiklerden ve başka gerekli reaktiflerden çıkarak nasıl sentezlersiniz?

(a) 1,10-Dekandiolden $(CH_3)_3\overset{+}{N}(CH_2)_{10}\overset{+}{N}(CH_3)_3 \; 2Br^-$

(b) Süksinik asit, 2-bromoetanol ve trimetilaminden başlayarak süksinilkolin bromür (bkz. bölüm girişi).

20.35 (a) $HOCH_2(CH_2)_8CH_2OH \xrightarrow{2\ PBr_3} BrCH_2(CH_2)_8CH_2Br \xrightarrow{2(CH_3)_3N}$

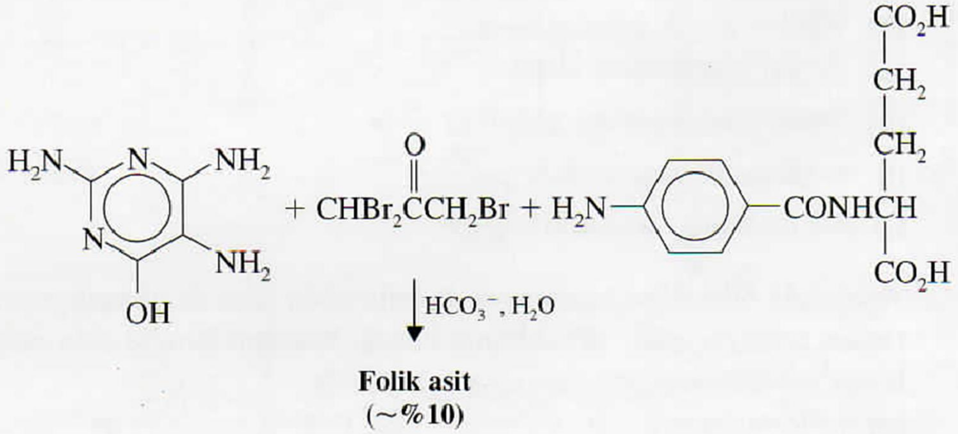
$(CH_3)_3\overset{+}{N}CH_2(CH_2)_8CH_2\overset{+}{N}(CH_3)_3\ \ 2\ Br^-$

(b) $HO_2CCH_2CH_2CO_2H + 2\ BrCH_2CH_2OH \xrightarrow[(-2\ H_2O)]{H^+}$

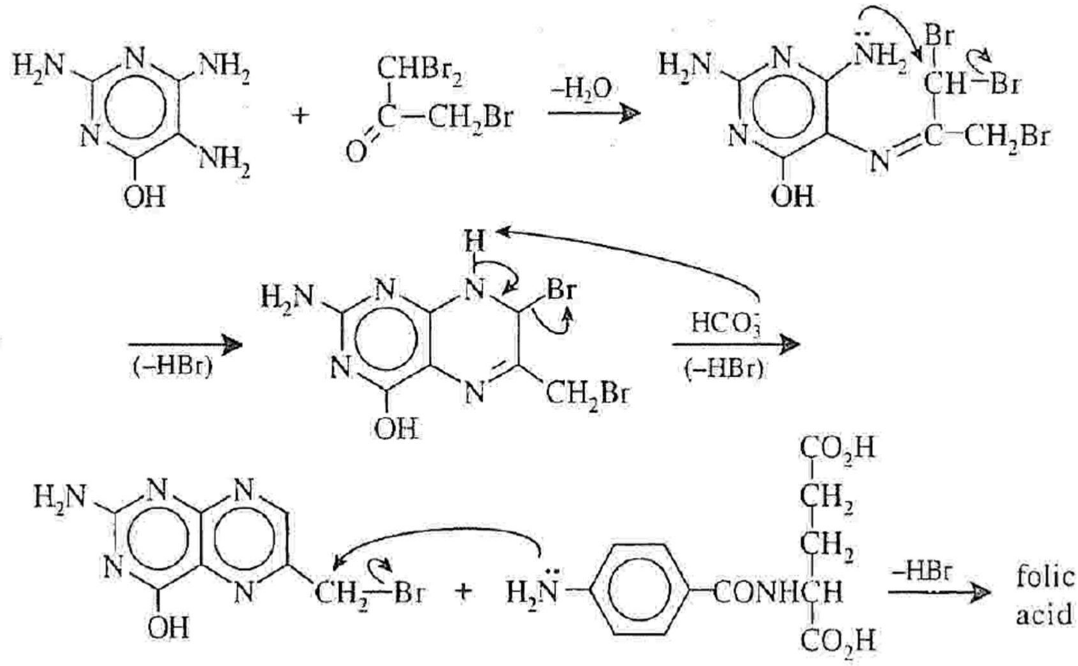
$BrCH_2CH_2O_2CCH_2CH_2CO_2CH_2CH_2Br \xrightarrow{2(CH_3)_3N}$

$(CH_3)_3\overset{+}{N}CH_2CH_2O_2CCH_2CH_2CO_2CH_2CH_2\overset{+}{N}(CH_3)_3\ \ 2\ Br^-$

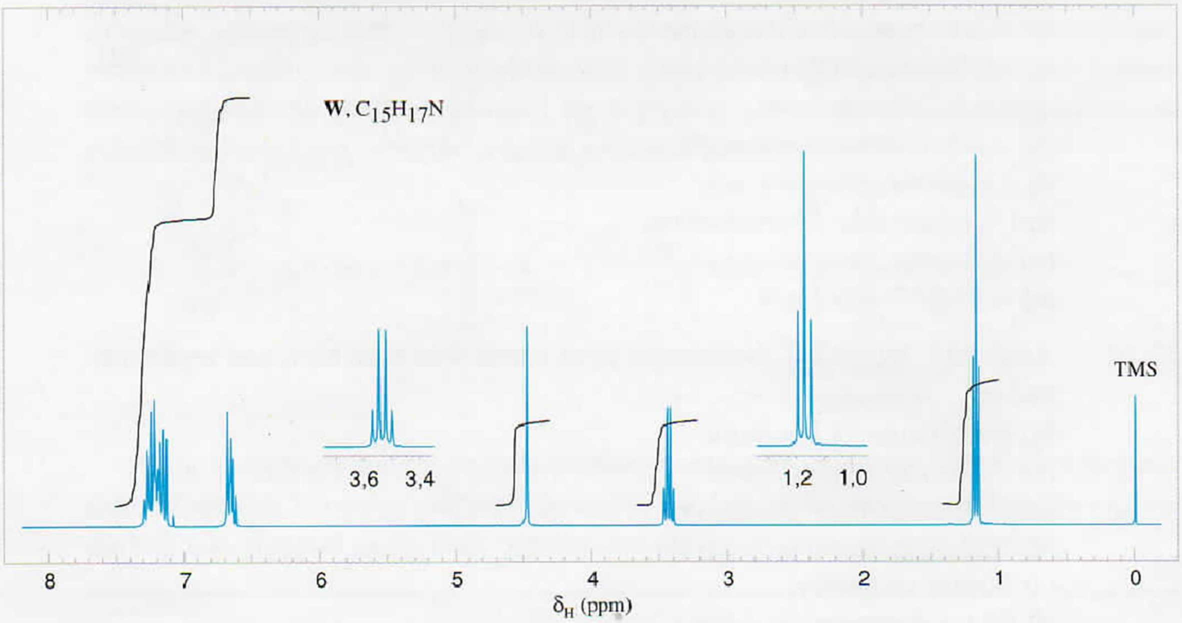
20.36 Folik asitin ticari sentezinde aşağıdaki üç bileşik sulu sodyum bikarbonat ile ısıtılır. Folik asit veren bu tepkimeler için uygun mekanizmalar öneriniz.



20.36



20.37 **W** bileşiği ($C_{15}H_{12}N$) benzensülfonil klorür ve sulu potasyum hidroksitle etkileştirildiğinde belirgin bir değişim gözlenmez. Bu karışımın asitlendirilmesi berrak bir çözelti verir. **W**'nun ^1H NMR spektrumu Şekil 20.7'de görülmektedir. **W** için bir yapı öneriniz.

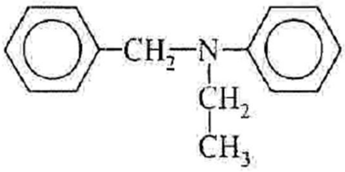


Şekil 20.7 **W bileşiğinin 300 MHz ^{1}H NMR spektrumu, Problem 20.37. Sinyallerin genişletilmiş şekilleri kaydırılmış olarak ayrıca gösterilmiştir.**

20.37 The results of the Hinsberg test indicate that compound **W** is a tertiary amine. The ^{1}H NMR provides evidence for the following:

(1) Two different C_6H_5–groups (one absorbing at δ 7.2 and one at δ 6.7).
(2) A CH_3CH_2–group (the quartet at δ 3.5 and the triplet at δ 1.2).
(3) An unsplit $-CH_2-$group (the singlet at δ 4.5).

There is only one reasonable way to pull all of this together.

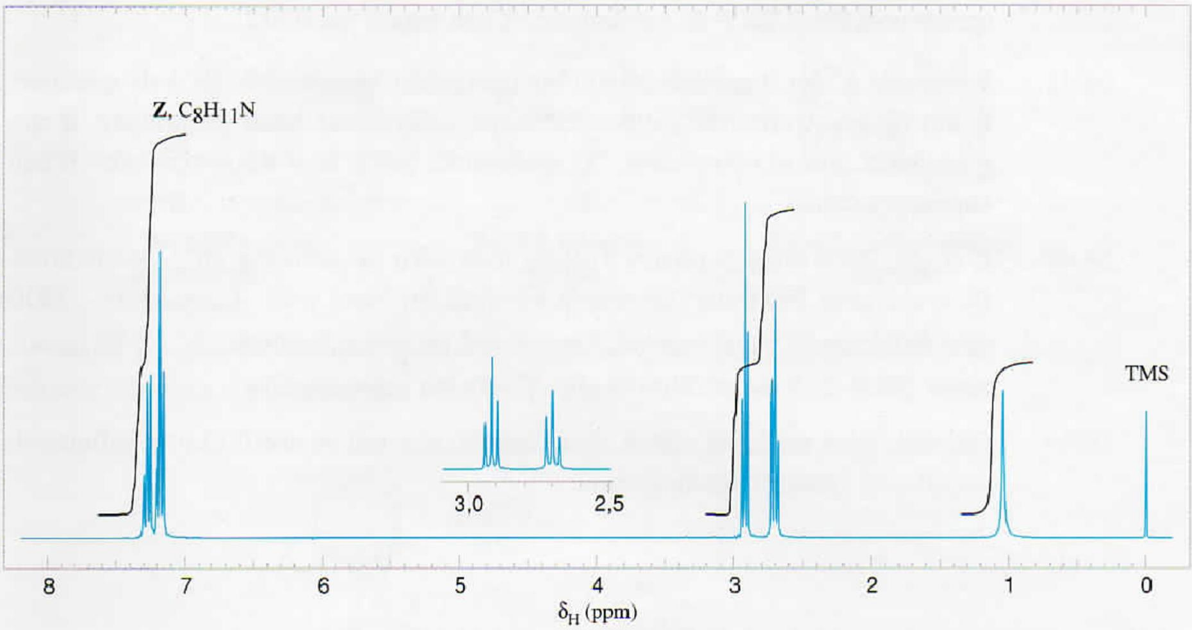


Thus **W** is *N*-benzyl-*N*-ethylaniline.

20.38 **X, Y** ve **Z** nin yapıları nasıldır?

$$\mathbf{X}\ (C_7H_7Br) \xrightarrow{NaCN} \mathbf{Y}\ (C_8H_7N) \xrightarrow{LiAlH_4} \mathbf{Z}\ (C_8H_{11}N)$$

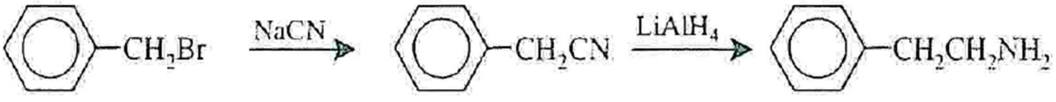
X'in ^{1}H NMR spektrumu δ 7,3'te çoklu (5H) ve δ 4,25'te birli (2H) olmak üzere iki sinyal verir. **X**'in İR spektrumu 680 – 840 cm^{-1} aralığında 690 cm^{-1} ve 770 cm^{-1}'de piklere sahiptir. **Y**'nin ^{1}H NMR spektrumu **X**'inkine benzer: δ 7,3'te çoklu (5H), δ 3,7'de (2H) birli (2H). **Z**'nin ^{1}H NMR spektrumu Şekil 20.8'de görülmektedir.



Şekil 20.8 **Z bileşiğinin 300 MHz ^{1}H NMR spektrumu, Problem 20.38. Sinyallerin genişletilmiş şekilleri kaydırılmış olarak ayrıca gösterilmiştir.**

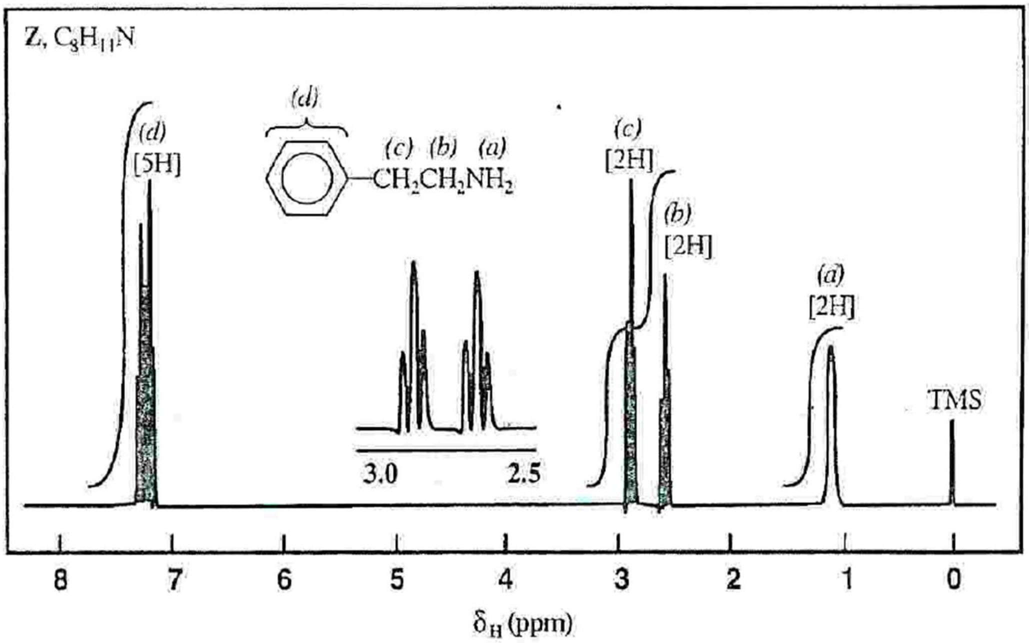
20.38 Compound **X** is benzyl bromide, $C_6H_5CH_2Br$. This is the only structure consistent with the ^{1}H NMR and IR data. (The monosubstituted benzene ring is strongly indicated by the (5H), δ 7.3 ^{1}H NMR absorption and is confirmed by the peaks at 690 and 770 cm^{-1} in the IR spectrum.)

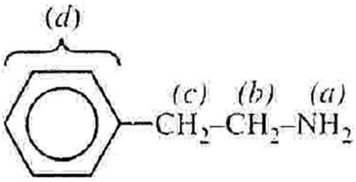
Compound **Y**, therefore, must be phenylacetonitrile, ($C_6H_5CH_2CN$) and **Z** must be 2-phenylethylamine, $C_6H_5CH_2CH_2NH_2$.



X C_7H_7Br **Y** C_8H_7N **Z** $C_8H_{11}N$

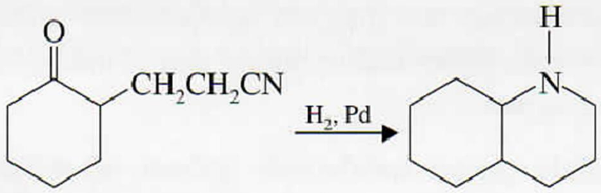
Interpretations of the IR and ^1H NMR spectra of **Z** are as follows.



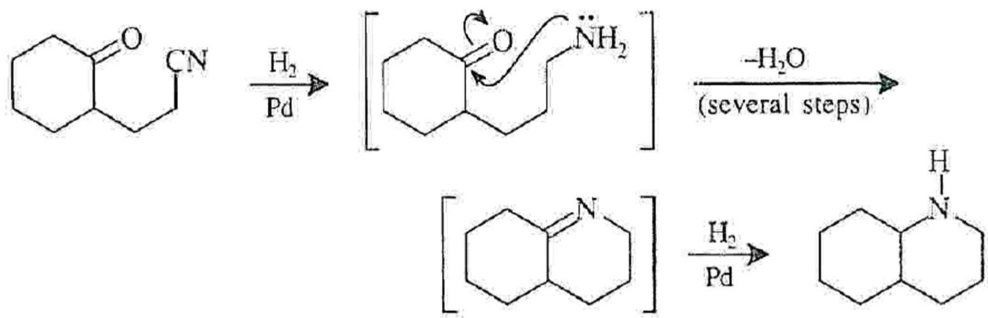


(*a*) singlet δ 1.0
(*b*) triplet δ 2.7
(*c*) triplet δ 2.9
(*d*) multiplet δ 7.25

20.39 Aşağıdaki tepkimeye bu bölümde öğrendiğiniz tepkimelerden yararlanarak bir mekanizma öneriniz?



20.39

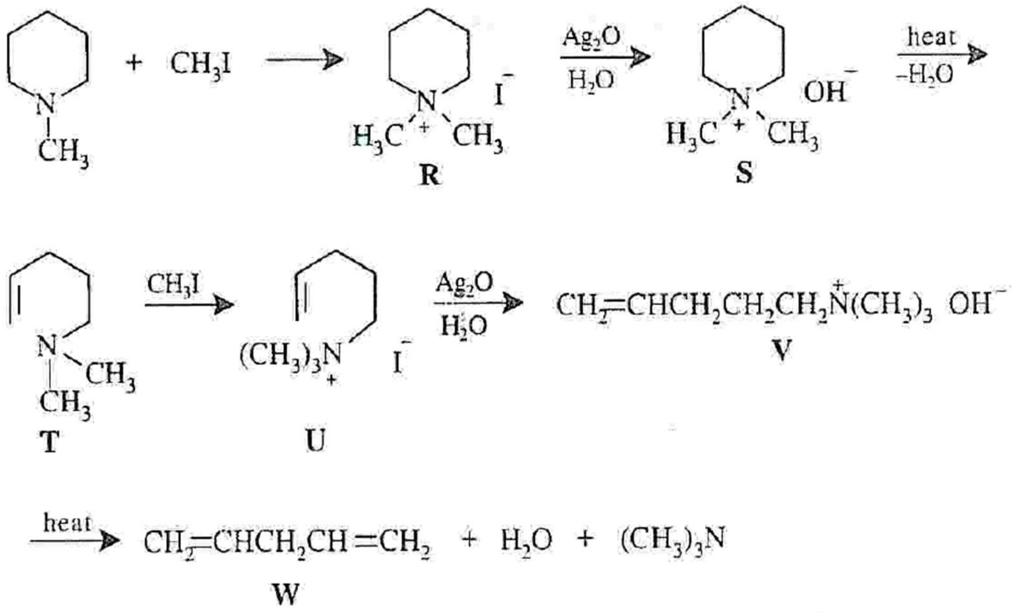


20.40 **R – W** bileşiklerinin yapılarını yazınız:

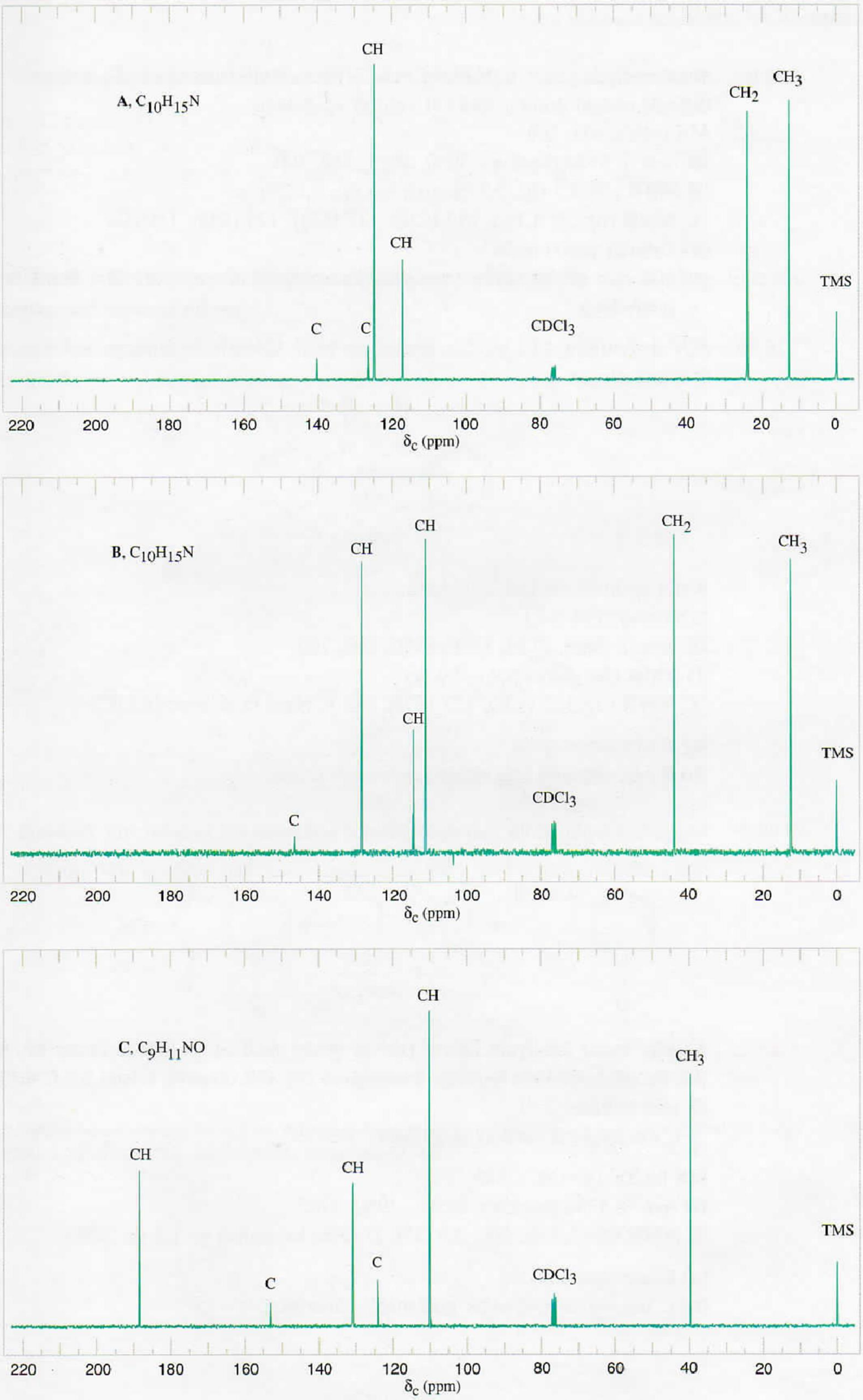
$$N\text{-Metilpiperidin} + CH_3I \longrightarrow \mathbf{R}\ (C_7H_{16}NI) \xrightarrow[H_2O]{Ag_2O} \mathbf{S}\ (C_7H_{17}NO) \xrightarrow[(-H_2O)]{\text{ısı}}$$

$$\mathbf{T}\ (C_7H_{15}N) \xrightarrow{CH_3I} \mathbf{U}\ (C_8H_{18}NI) \xrightarrow[H_2O]{Ag_2O} \mathbf{V}\ (C_8H_{19}NO) \xrightarrow{\text{ısı}} \mathbf{W}\ (C_5H_8) + H_2O + (CH_3)_3N$$

20.40

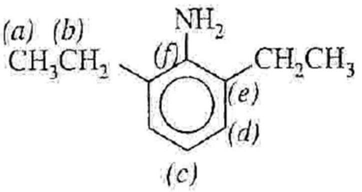


20.41 **A** ($C_{10}H_{15}N$) bileşiği seyreltik HC1'de çözünür İR soğurma spektrumu 3300 – 3500 cm^{-1} bölgesinde iki band verir. **A**'nın genişband proton-eşleşmesiz ^{13}C spektrumu Şekil 20.9'da verilmiştir. **A**'nın yapısı nasıldır?



Şekil 20.8 Problem 20.41 – 20.43'teki A, B ve C bileşiklerinin genişband proton-eşleşmesiz ^{13}C NMR spektrumları. DEPT ^{13}C NMR spektrumlarından elde edilen bilgiler her pikin üzerinde verilmiştir.

20.41 That **A** contains nitrogen and is soluble in dilute HCl suggests that **A** is an amine. The two IR absorption bands in the 3300–3500-cm^{-1} region suggest that **A** is a primary amine. The ^{13}C spectrum shows only two signals in the upfield aliphatic region. There are four signals downfield in the aromatic region. The information from the DEPT spectra suggests an ethyl group *or two equivalent ethyl groups.* Assuming the latter, and assuming that **A** is a primary amine, we can conclude from the molecular formula that **A** is 2,6-diethylaniline. The assignments are

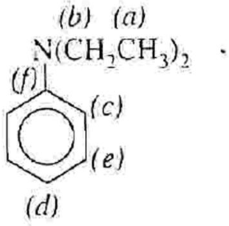


(a) δ 12.9
(b) δ 24.2
(c) δ 118.1
(d) δ 125.9
(e) δ 127.4
(f) δ 141.5

(An equally plausible answer would be that **A** is 3,5-diethylaniline.)

20.42 **B** bileşiği **A**’nın (Problem 20.41) bir izomeridir ve seyreltik HCl’de çözünür. **E**’nin İR spektrumunda 3300 – 3500 cm^{-1} bölgesinde band gözlenmez. **B**’nin genişband proton-eşleşmesiz ^{13}C spektrumu Şekil 20.9’da verilmiştir. **B**’nin yapısını yazınız.

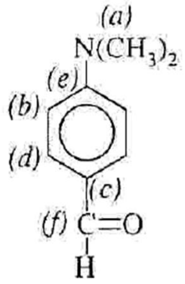
20.42 That **B** dissolves in dilute HCl suggests that **B** is an amine. That the IR spectrum of **B** lacks bands in the 3300–3500-cm^{-1} region suggests that **B** is a tertiary amine. The upfield signals in the ^{13}C spectrum and the DEPT information suggest two equivalent ethyl groups (as was also true of **A** in the preceding problem). The DEPT information for the downfield peaks (in the aromatic region) is consistent with a monosubstituted benzene ring. Putting all of these observations together with the molecular formula leads us to conclude that **B** is *N,N*-diethylaniline. The assignments are



(a) δ 12.5
(b) δ 44.2
(c) δ 112.0
(d) δ 115.5
(e) δ 128.1
(f) δ 147.8

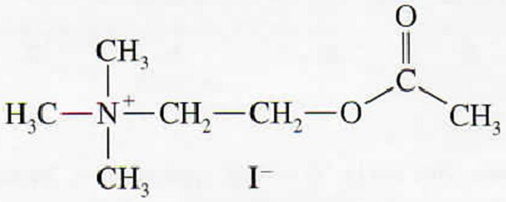
20.43 **C** ($C_9H_{11}NO$) bileşiği pozitif Tollens testi verir ve seyreltik HCl’de çözünür. İR spektrumu 1695 cm^{-1} civarında kuvvetli bir band verir, fakat 3300 – 3500 cm^{-1} bölgesinde band vermez. Genişband proton-eşleşmesiz ^{13}C NMR spektrumu Şekil 20.9’da görülmektedir. **C** için bir yapı öneriniz.

20.43 That **C** gives a positive Tollens' test indicates the presence of an aldehyde group: the solubility of **C** in aqueous HCl suggests that **C** is also an amine. The absence of bands in the 3300–3500-cm^{-1} region of the IR spectrum of **C** suggests that **C** is a tertiary amine. The signal at δ 189.7 in the ^{13}C spectrum can be assigned to the aldehyde group. The signal at δ 39.7 is the only one in the aliphatic region and is consistent with a methyl group or with two equivalent methyl groups. The remaining signals are in the aromatic region. If we assume that **C** has a benzene ring containing a $-\overset{\overset{\displaystyle O}{\|}}{C}H$ group and a $-N(CH_3)_2$ group, then the aromatic signals and their DEPT spectra are consistent with **C** being *p*-(*N*,*N*-dimethylamino)benzaldehyde. The assignments are



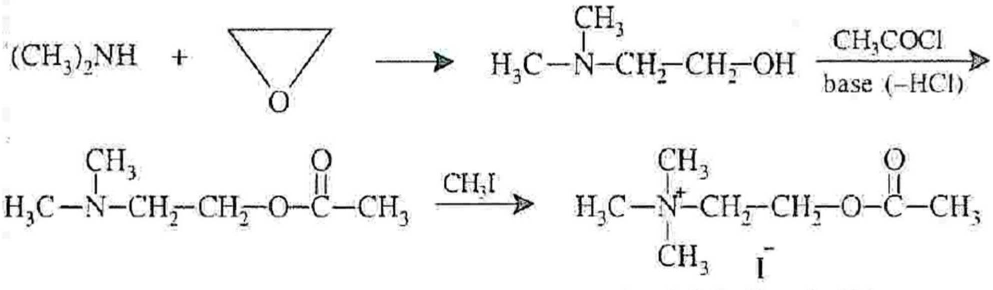
(*a*) δ 39.7
(*b*) δ 110.8
(*c*) δ 124.9
(*d*) δ 131.6
(*e*) δ 154.1
(*f*) δ 189.7

20.44 Organik çıkış maddesi olarak dimetilamin, oksiran ve asetil klorür kullanarak asetilkolin iyodürü sentezleyiniz.



Asetilkolin iyodür

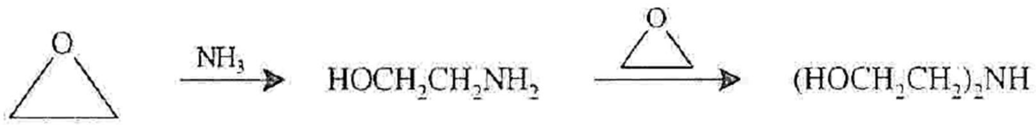
20.44



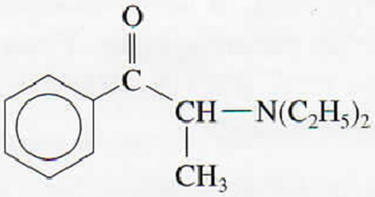
Acetylcholine iodide

20.45 Etanolamin, $HOCH_2CH_2NH_2$, ve dietanolamin, $(HOCH_2CH_2)_2NH$, emülsifiye edici bir madde oluşturmak ve asidik gazları soğurmak için ticari olarak kullanılır. Bu iki bileşiği nasıl sentezleyebilirsiniz?

20.45

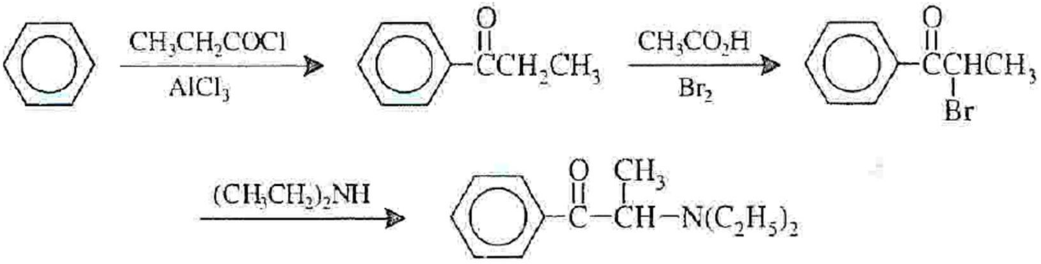


20.46 Dietilpropiyon (aşağıda verilen yapıya bakınız) anoreksiya tedavisinde kullanılan bir bileşiktir. Benzenden çıkarak ve gerekli maddeleri kullanarak dietilpropiyonun sentezini tasarlayınız.



Dietilpropiyon

20.46



Diethylpropion

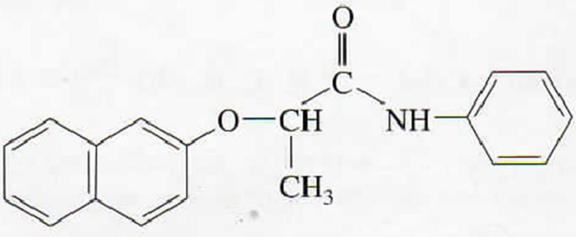
20.47 Hofmann tepkimesinin bir molekül içi çevrilme olduğunu, yani göçen R grubunun amit grubundan hiçbir zaman tam olarak ayrılmadığını kanıtlayan bir deney tasarlayınız.

20.47 Carry out the Hofmann reaction using a mixture of ^{15}N labeled benzamide, $C_6H_5CO{*}NH_2$, and *p*-chlorobenzamide. If the process is intramolecular, only labeled aniline, $C_6H_5{*}NH_2$, and *p*-chloroaniline, will be produced.

If the process is one in which the migrating moiety truly separates from the remainder of the molecule, then, in addition to the two products mentioned above, there should be produced both the unlabeled aniline and labeled *p*-chloroaniline, *p*-$ClC_6H_4{*}NH_2$.

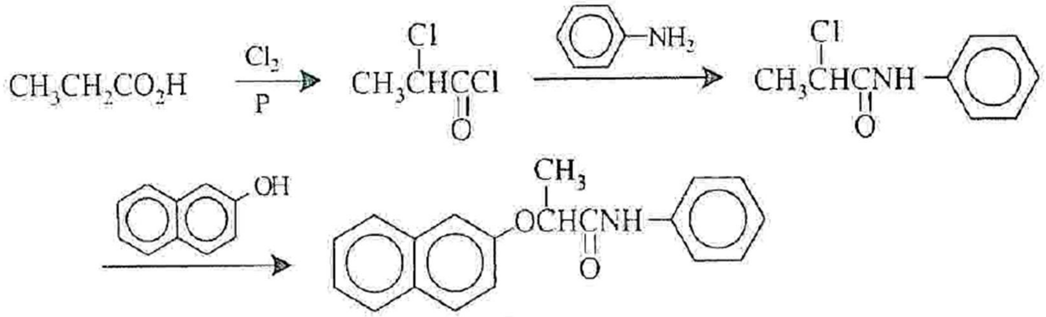
Note: When this experiment is actually carried out, analysis of the reaction mixture by mass spectrometry shows that the process is intramolecular.

20.48 Asya ülkelerinde pirinç tarlalarında yabani ot mücadelesinde kullanılan naproanilitin sentezini propanoik asit, anilin ve 2-naftolden çıkarak nasıl yapabilirsiniz?



Naproanilit

20.48



***20.49** Fenil izotiyosiyanat, $C_6H_5N{=}C{=}S$, lityum alüminyum hidrür ile indirgendiğinde oluşan ürünün spektral verileri aşağıdadır;

MS (m/z): 107, 106

IR (cm^{-1}): 3330 (keskin), 3050, 2815, 760, 700

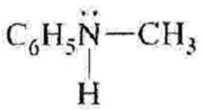
^{1}**H NMR** (δ): 2,7 (b), 3,5 (geniş), 6,6 (ç), 7,2 (ü)

^{13}**C NMR** (δ): 30 (CH_3), 112 (CH), 117 (CH), 129 (CH), 150 (C)

(a) Ürünün yapısı nedir?

(b) 106 m/z pikini veren yapı nasıldır ve nasıl oluşmuştur? (Bir iminyum iyonudur.)

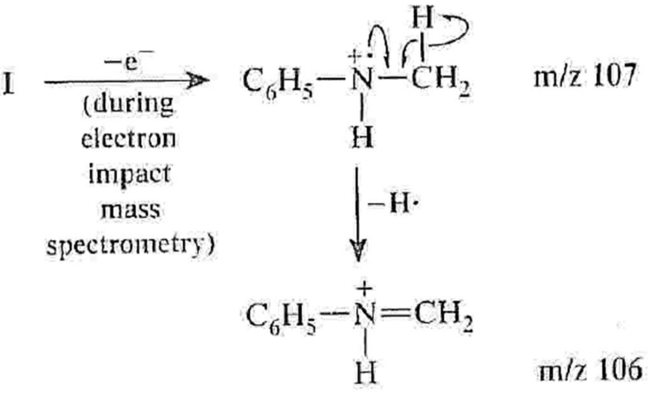
*20.49 (a)



$C_6H_5\underset{H}{\underset{|}{\ddot{N}}}-CH_3$

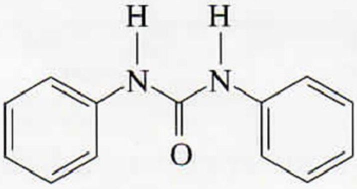
I

(b)



I
$-e^-$
(during electron impact mass spectrometry)
$C_6H_5-\overset{+\cdot}{N}-CH_2$
H
H
m/z 107
$-H\cdot$
$C_6H_5-\overset{+}{N}{=}CH_2$
H
m/z 106

***20.50** *N,N'*-Difenilüre (**A**) piridin içerisinde tosil klorürle tepkimeye sokulunca **B** ürünü oluşur.



A

B'nin spektral verileri aşağıdadır:

MS (m/z): 194 ($M^{+\cdot}$)

IR (cm^{-1}): 3060, 2130, 1590, 1490, 760, 700

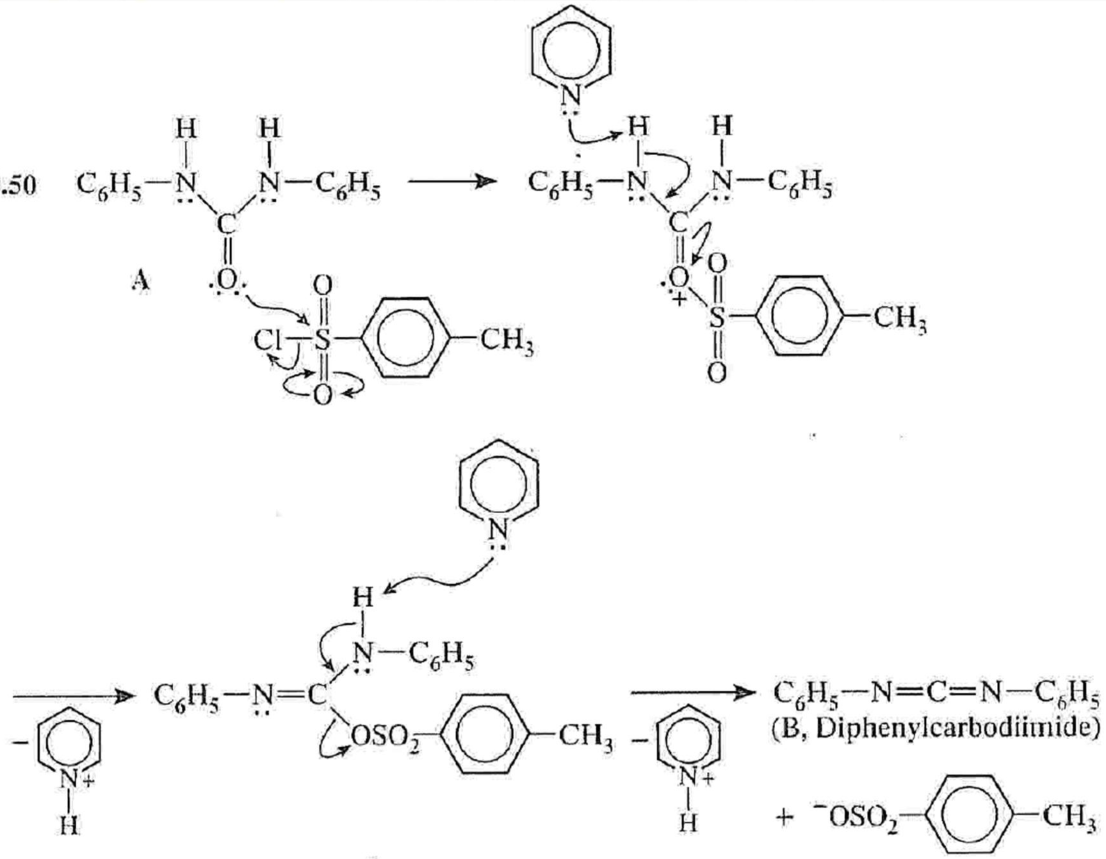
^{1}**H NMR** (δ): yalnız 6,9 – 7,4 (ç)

^{13}**C NMR** (δ): 122 (CH), 127 (CH), 130 (CH), 149 (C), ve 163 (C)

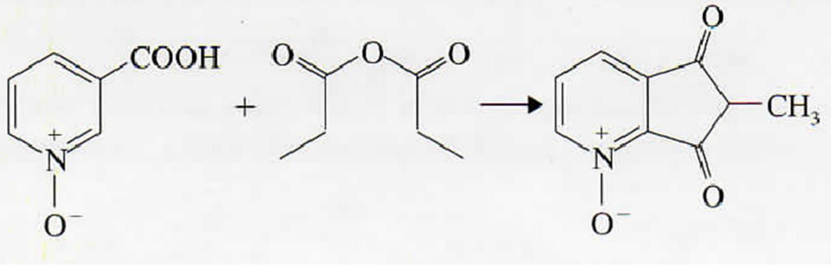
(a) **B**'nin yapısı nedir?

(b) **B**'nin oluşumu için bir mekanizma öneriniz.

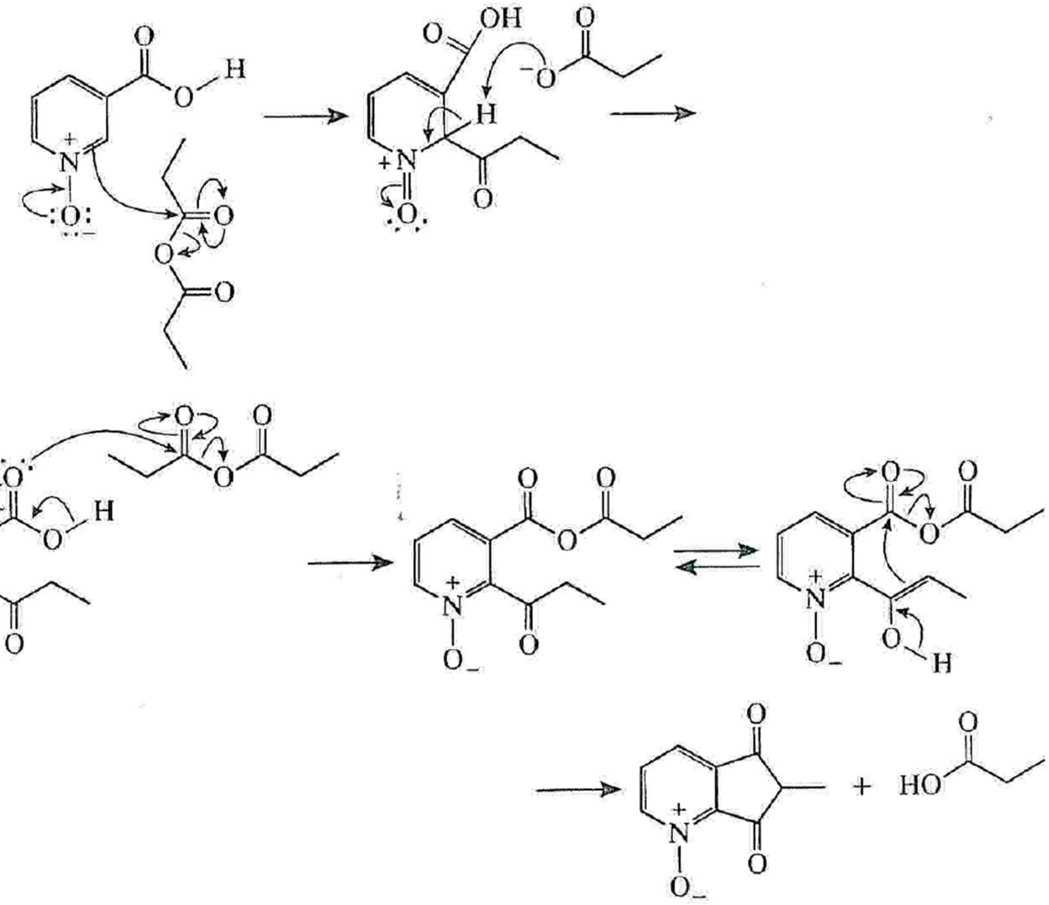
*20.50



*** 20.51** Aşağıdaki tepkimenin meydana gelişini açıklayan bir mekanizma öneriniz.



*20.51



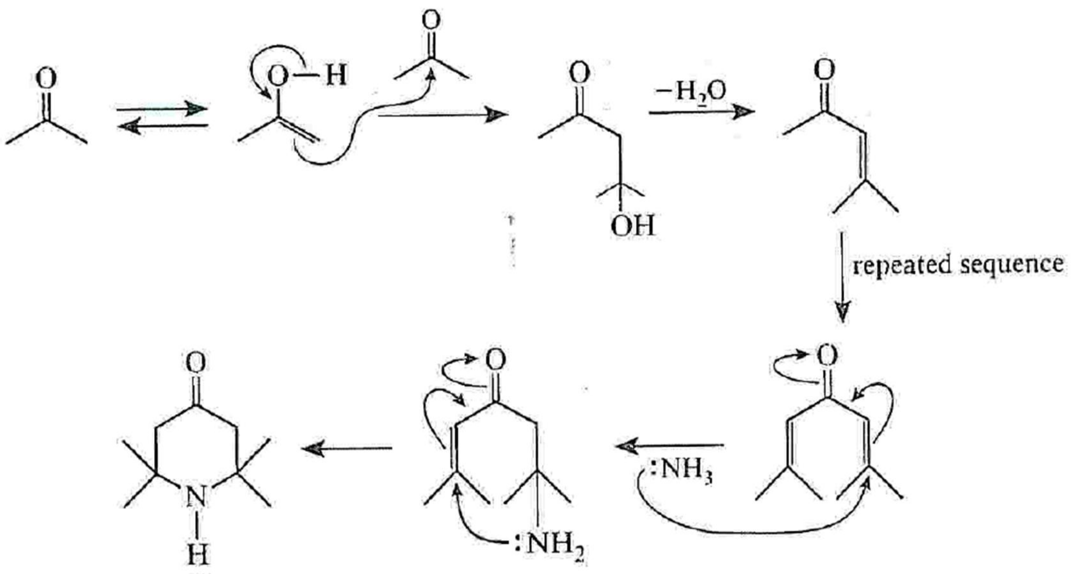
***20.52** Aseton, susuz kalsiyum klorür (bir su çekici madde) içerisinde susuz amonyak ile etkileştirilirse tepkime karışımının organik fazında, kristal bir **C** ürünü elde edilir.

C'nin spektral verileri aşağıdadır:

MS (m/z): 155 ($M^{+\cdot}$), 140
IR (cm^{-1}): 3350 (keskin), 2850 – 2960, 1705
^{1}H NMR (δ): 2,3 (b, 4H), 1,7 (1H; D_2O'da kaybolur) ve 1,2 (b, 12H)

(a) **C**'nin yapısı nedir?
(b) **C**'nin oluşumu için bir mekanizma öneriniz.

***20.52** An abbreviated version of one of several possible routes:

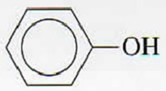


C

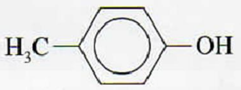
"triacetoneamine"

Fenoller ve Aril Halojenürler: Nükleofilik Aromatik Yer Değiştirme

Problem 21.1 ➤ Çizelge 21.2'yi incelediğimizde metilfenollerin (krezoller) fenolün kendisinden daha zayıf asit olduklarını görürüz.



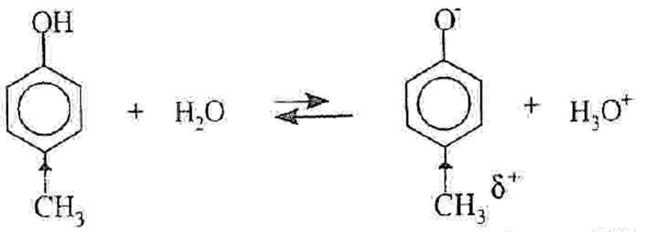
Fenol
pK_a = 9,89



4-Metilfenol
pK_a = 10,17

Bu davranış, elektron veren grupları taşıyan fenoller için özgüdür. Buna bir açıklama getiriniz.

21.1 An electron-releasing group (i.e., $-CH_3$) changes the charge distribution in the molecule so as to make the hydroxyl oxygen less positive, causing the proton to be held more strongly; it also destabilizes the phenoxide anion by intensifying its negative charge. These effects make the substituted phenol less acidic than phenol itself.



Electron-releasing $-CH_3$ destabilizes the anion more than the acid—pK_a is larger than for phenol.